

Polymer

ENGINEERING AND SCIENCE

POLYMER TOPICS

Modeling—'84
National Research Council of Canada
Industrial Materials Research Institute

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Polymer

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GUEST EDITORS—L. A. UTRACKI

ASSOCIATE EDITOR—RICHARD E. BALL

*% Polymer Science and Engineering
University of Massachusetts
Amherst, Mass. 01003*

*% Industrial Materials Research Institute
National Research Council of Canada
75, Boul. De Mortagne
Boucherville, Quebec J4B 6Y4
Canada
and*

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OPENING REMARKS: WHITHER MODELING

Having read through the preprints of the meeting, I have the impression that this is a somewhat *monastic* exercise: we are getting increasingly secluded from *temporal* concerns and inclining more and more to *religion*. The mathematics we use is becoming exceedingly complex, the number of named models and constitutive equations is rapidly multiplying and we are trying to coax our infinite series into convergence (1). It looks like we are searching for the medieval "philosophers' stone" to solve all our problems via universally applicable models, applicable to all polymers and conditions.

The material we are working with, however, is complex. There are no two molecular chains alike. Millions of them exist in every cubic centimeter, and the possibilities of association, one with another, are infinite.

During the late sixties and early seventies, a number of flow models were developed for simple cavities using one-dimensional, nonisothermal flow, involving Power-Law fluids. But one of my colleagues tells me that it took 67 person-years to develop from this a suitable computer program for practical CAD/CAM/CAE use. That software is an excellent program for predicting filling times, pressure distribution and short shots in injection molding, and for balancing multi-cavity molds. But 67 person-years correspond to \$2-1/2 million in salaries alone if graduate professionals were involved—and this is only a modest beginning toward practical applications. We have to think of more economical approaches to modeling.

I could think of a more *interdisciplinary* approach. Maybe we could use equations applicable to only a very limited range of data and match these curves with the actual data obtained during the process, in real time. And then again repeat the process as experimental data change in a dynamic mode and fit a new curve, and keep iterating. Perhaps we should meet with the physicists—they have made impressive advances in nondestructive testing. Just to give you one example, we now have

a technique to measure the density of polymers to four decimals without physical contact (2). Density at a given pressure can be a measure of crystallinity, which again depends on thermal history. The cavity filling could be observed using ultrasonic scanning techniques. This could give us actual flow rate data, in real time. Electronic data processing is becoming less and less expensive every year—as the mathematics is being simplified to minimize programming. This might permit us to treat the actual data in a quasi-phenomenological manner. Then maybe we can forget about the underlying analogue relationship between the physical phenomena and the corresponding mathematical functions. With the configurational multitude of macromolecules maybe no simple mathematical function is available, as there is no simple physical model either.

The scientist's task is to understand, but the engineer's task is to get things done. The scientific understanding is a *sacred* task, and as a scientist, I hesitate to do away with it. But the engineer's world is *temporal*: it is limited by time and it pertains to this world, and to present life. Our practical problems in plastics processing are "here and now", as Aldous Huxley's birds were singing it on his enchanted island.

I urge you to look and to step outside of our *monastery* of mathematical modeling, as it is constituted now—and please look for short cuts.

George L. Bata
Director
Industrial Materials Research Institute
National Research Council Canada

REFERENCES

1. Kamal, M. R. and G. L. Bata, Current Trends in the Analysis of Polymer Shaping Operations, Presented at the European Meeting on Polymer Processing and Properties, Capri, Italy, June 12-16, 1983.
2. L. Piché, Industrial Materials Research Institute, NRCC, Montréal, Canada, private communication.

EDITORS' NOTE

The seven papers published in this issue of *Polymer Engineering and Science* were presented January 24th, 1984, during the third mini-symposium on "Mathematical Modeling of Plastics Processing Operations and Polymer Properties" in a series on "Modeling", organized and sponsored by the Industrial Materials Research Institute of the National Research Council of Canada. The Institute is located in Boucherville, Quebec, across the St. Lawrence River from Montreal. Two other symposia series, "Polyblends" and "Composites", are being held annually in the Institute, respectively, each April and November.

These symposia are intended to serve as focal points to facilitate the communication and exchange of ideas, primarily within the Canadian technical community. By providing an appropriate interface for research scientists working in academia, government and industry, it is hoped that a meaningful dialogue can be encouraged and established. The benefits of this exchange may enhance collaborative research efforts, promote better understanding, and stimulate technology transfer.

The first three papers provide more basic information. Utracki discussed the use of the equation of state in describing the pressure and temperature effects on melt viscosity—a subject of particular importance in modeling injection molding. Carreau, *et al.*, as well as Mitsoulis, *et al.*, deal with the mathematical description of die flow phenomena: prediction of entry vortices, rheological sources of exit pressure drop, and computation of extrudate swell.

The following three papers deal with various aspects of plastics processing and control. The relation between melt rheology and extrusion parameters is discussed by Utracki and Catani. The modeling of the film embossing process by Kamal, Haber, and Ryan is a first attack on this difficult problem. In the final paper of the symposium, Fara, Kamal, and Patterson evaluate various means of control of the injection-molding process.

In addition to the technical papers, a less formal panel discussion relating to the role and utility of mathematical modeling to commercial polymer processes has been organized and included in the program. The intent was to provide an open and candid forum for elucidating current activity with regard to the development, evaluation, and application of mathematical models to industrial operations. This includes work done "in-house" as well as case study evaluation and use of "commercially-available" process models and CAD/CAM programs.

The proceedings of the meeting were recorded. A transcript of the discussions is provided at the end of each paper. Interested parties are welcome to listen to the tapes which are deposited for two years in the Institute Library.

As organizers of the symposium we wish to express our thanks to the authors, the "vocal" participants, and to the Editor of this journal for making "Modeling-'84" a success.

Michael E. Ryan and L. A. Utracki
Organizers and guest editors

A Method of Computation of the Pressure Effect on Melt Viscosity

L. A. UTRACKI

National Research Council of Canada
Industrial Materials Research Institute
75 De Mortagne Blvd
Boucherville, Quebec J4B 6Y4

Simha's equation of state provides the relation between: reduced pressure, temperature, and volume ($\bar{P}$, $\bar{T}$, and $\bar{V}$, respectively) and the occupied site fraction, $y = y(\bar{P}, \bar{T})$. The latter theoretical parameter combines the P and T effects on the occupied and unoccupied ("free volume") part of the model liquid. It can be computed for each liquid once the thermodynamic reducing parameters are known. Empirical correlation between published zero shear viscosity data, $\eta = \eta(P, T)$, and y indicates that for n -paraffins and molten polymers η is a single parameter function: $\eta = \eta(y)$. The mathematical form of this dependence was explicitly given for n -paraffins. However, for polymers the correlation depends on molecular weight, molecular weight distribution, branching, composition, etc. In practical terms, $\eta = \eta(y)$ should be determined for each polymer by measuring the temperature dependence of η in as wide a range of T as possible. Then pressure effect on η can be determined from $\eta = \eta(y)$ plot, knowing the $y = y(\bar{P}, \bar{T})$ relation.

INTRODUCTION

The mathematical modeling of plastics processing involves iterative multi-variable computations (1 to 3). The inherent complexity of the method, as well as the scarcity of rheological data, leads to gross oversimplification of the polymer flow properties. Even now there are models incorporating the zero-shear viscosity, η , as the single rheological parameter. In the more sophisticated ones, the rate-of-shear, $\dot{\gamma}$, and the temperature, T , dependencies of viscosity, are introduced via the "power law" and Arrhenius equations respectively:

$$\ln \eta_i = \ln \eta(\dot{\gamma} = 1) - (1 - n) \ln \dot{\gamma} \quad (1)$$

$$(\partial \ln \eta) / (\partial (1/T))|_{P=0} = E_a/R \quad (2)$$

Only in the most advanced models of injection molding is the pressure, P , effect also incorporated using the Cogswell simplification (4):

$$(\partial \ln \eta / \partial P)_T = K(T)E_a \quad (3)$$

The temperature dependent K has to be determined experimentally for each polymer.

There are questions as to the extent of the pressure effect and the size of the error should it be neglected. The demand for a better product, the need for faster production, and resulting advances in processing equipment continuously increase the operating pressures. In extrusions and injection

molding, the pressures are up to 50 and 700 MPa respectively. How much these pressures influence η depends on the relative temperature. Since P increases both the melting point, T_m , and the glass transition temperature, T_g , the effect can be truly dramatic (4 to 6); a thousand-fold increase in η for polystyrene (PS) was reported increasing P from 0.1 to 100 MPa.

HISTORICAL DEVELOPMENT

During the last few years, an effort has been made to seek the general form of η -behavior of polymeric and nonpolymeric liquids as functions of T and P (6 to 12). The work has been based on the free volume approach.

The isobaric T -effect has been successfully discussed on the basis of the Doolittle equation:

$$\ln \eta = A_0 + B_0 Y_D \quad (4)$$

where

$$Y_D = [(V - V_0)/V_0]^{-1},$$

A_0 and B_0 are equation constants, while V and V_0 are molar or specific volumes at T and at $T = 0(K)$, respectively. The V and V_0 can be computed from the semi-empirical relation (13):

$$\ln \bar{V} = S_0 + S_1 \bar{T}^{3/2} \quad (5)$$

where S_0 and S_1 are parameters and symbols with

the tilde indicating the reduced variables:

$$\tilde{F} = F/F^*, \text{ where } F = V, T \text{ or } P,$$

with F^* 's being the scaling thermodynamic parameters of the liquid. Assuming the effective occupied volume fraction $V_{o,eff} \geq V_o$, as defined in Eq 4, the hydrodynamic shielding parameter was defined as:

$$h = V_o/V_{o,eff} \quad (6)$$

From Eqs 4 to 6, the temperature dependence of liquid viscosity was predicted to follow the linear dependence:

$$\ln \eta = A + BY \quad (7)$$

where A and B are parameters, and

$$Y = 1/[h \exp \{0.11515 (T/T_g)^{3/2} - 1\}].$$

It has been shown that Eq 7 is obeyed by all evaluated liquids including: water, paraffins, aromatics, alcohols, aldehydes, liquified noble gasses, liquid metals, inorganic glasses, polymer melts, etc. (7 to 9). The adequacy of Eq 7 to describe the concentration effect of the polymer solution viscosity was also demonstrated (9).

The usefulness of the Doolittle equation and in consequence Eq 7 disappears when P -effects are concerned (6). If Eq 4 is directly used, instead of a single straight line dependence: $\ln \eta$ versus Y_D , a series of isothermal curves are obtained. If Eq 7 is applied then again the data do not superimpose, and the value of $h > 1$ is required to linearize the dependence. The need to use $h \leq 1$ for isobaric and $h > 1$ for isothermic conditions negates the physical significance originally assigned to it.

Before proceeding further, it was necessary to test whether the accepted correlation between η and the free volume fraction, f , exists. Historically, the parameter f was defined (14) as:

$$f = V - \Omega \quad (8)$$

where Ω was determined by the condition:

$$\lim_{V \rightarrow \Omega} \eta = \infty. \quad (9)$$

In the original work (14), it was observed that for nonpolymeric liquids:

$$V_s < \Omega < V_o$$

where V_s is the molar or specific volume in the crystalline state. A more precise relation was found between Ω and the critical volume, V_K :

$$3 \Omega/V_K = \Omega/b = 0.921 \pm 0.018 \quad (10)$$

where b is the van der Waals constant. Since the critical conditions represent a reference point, $P_K V_K/T_K = \text{const}$, it was postulated that Ω can be computed from the equation of state. It is this fundamental principle, the correlation between the transport function, η , and the thermodynamic equation of state quantity, f , which needs to be examined.

In the recent paper (12), the relation between the experimental $\eta = \eta(P, T)$ and the theoretical

function $f = f(P, T)$, computed from an equation of state, for n -paraffins C_5 to C_{18} was examined. While the results confirmed Batschinski's basic hypothesis, at the same time they demonstrated that neither his nor Doolittle's form of the equation is correct. The data for all n -paraffins examined so far could be described by the relation:

$$\ln \eta/\eta^* = A_1 + B_1/(f + \Delta) \quad (11)$$

where η^* is the vertical shift parameter and A_1, B_1 , and $\Delta = 0.070$ are constants of the equation.

In the last publication of this series (15), the applicability to polymeric liquids of the treatment developed for n -paraffins was examined. Four liquids: oligomeric silicone oil, poly(dimethyl siloxane), polypropylene, and low density polyethylene, or in brief: SiOil, PDMS, PP, and LDPE, respectively, were evaluated. In all but the last case, a single sample was examined. The data in full range of T and P did superimpose on a single curve. There was no effort made to develop an empirical equation between η and f for these samples. However, the general shape of the dependence indicated that Eq 11, (possibly with different values of $\Delta \geq 0$) could be used.

For LDPE, there were two sets of data. While in each set $\eta(P, T)$ seemed to follow a single $\eta = \eta(f)$ dependence, these differed for the two sets. The difference was particularly large at large f . As f decreased, the two sets (excepting the samples partially crystallized under pressure) seem to collapse into a single curve; $\eta \approx 10^7$ (Pa.s). This could be taken as an indication that effects of the molecular weight, polydispersity, and structure are losing their importance under high pressure.

In the present paper, the details of the computational procedure for SiOil, PDMS, PP, and LDPE will be examined. The procedure will be applied to additional sets of $\eta(P, T)$ data available from the literature. A simple procedure to compute the pressure effects on viscosity will be proposed.

EQUATION OF STATE

The Simha-Somcynsky equation of state (16) has been successfully used in describing P - V - T relations for numerous polymeric and nonpolymeric liquids, as well as liquid mixtures (13, 17 to 28). For polymeric liquids, the general equations can be simplified to read:

$$\tilde{P}\tilde{V}/\tilde{T} = [1 - 2^{-1/6} y \phi^{1/3}]^{-1} + (2y/\tilde{T}) \phi^2 [1.011 \phi^2 - 1.2045] \quad (12)$$

$$[1 + y^{-1} \ln(1 - y)] = (y/6\tilde{T}) \phi^2 [2.409 - 3.033 \phi^2] + [2^{-1/6} y \phi^{1/3} - 1/3] \cdot [1 - 2^{-1/6} y \phi^{1/3}]^{-1} \quad (13)$$

where:

$$\phi = 1/(y\tilde{V}) \text{ and } y = 1 - f.$$

To compute $f(\tilde{P}, \tilde{T})$ from the coupled Eqs 12 and 13, first the reducing parameters, F^* 's, have to be determined. Once these are known, then for each

T Eqs 12 and 13 can be solved. The computation starts by setting $\tilde{P} = 0$, to determine the initial values of $\tilde{V}$, y , and $Y_s = 1/(1-y)$. Next, the coupled equations are solved for $\tilde{P}$, y , and Y_s at constant, selected intervals: $\delta = \ln(\tilde{V}_{i+1}/\tilde{V}_i)$. To determine Y_s at the appropriate, experimental value of P , a polynomial interpolation method is used. As a result, to each experimental data point $\eta(P_i, T_i)$ a corresponding packing parameter $Y_s(P_i, \tilde{T}_i)$ (per definition $\tilde{P}_i = P_i/P^*$ and $\tilde{T}_i = T_i/T^*$) is assigned.

The method of determination of the reducing parameters was detailed previously (12). Briefly, for polymer melts the method involves two steps: determination of V^* and T^* from the isobaric V - T data, and computation of P^* . In the first step, one makes use of the approximate Eq 5 with $S_0 = -0.10335$ and $S_1 = 23.8345$ (6). The values of $\tilde{V}$ computed from Eq 5 are within 0.16 percent of those computed directly from the coupled Eqs 12 and 13 at $\tilde{P} = 0$ in the range: $1.65 \leq \tilde{T} \cdot 10^2 \leq 7.03$. Comparing the experimental values of the parameters in the empirical dependence:

$$\ln V = Z_0 + Z_1 T^{3/2}, \quad (14)$$

with S_0 and S_1 , one finds that:

$$V^* = \exp \{Z_0 - S_0\}, \quad (15a)$$

and

$$T^* = (S_1/Z_1)^{2/3}. \quad (15b)$$

It should be stressed that the above quoted values of S_0 and S_1 were determined by solving Eqs 12 and 13 at $P = 0$. Obviously, V^* and T^* should not depend on the assumed isobaric conditions, as long as these are identical for V - T experiments and for the computation of S_0 and S_1 .

In the second step, $\tilde{V}$ and $\tilde{P}$ are computed from Eqs 12 and 13 at the experimentally defined $\tilde{T}_i = T_i/T^*$. Since V^* is known, then experimental values of $\tilde{V}_i = V_i/V^*$ are known and the corresponding $\tilde{P}_i$ can be determined. Since P_i (corresponding to T_i and V_i) is also known, then P_i^* can be computed from each P - V - T point. Usually, these P_i^* 's are averaged to obtain the final P^* value.

EVALUATION

SiOil

The viscosity, η , and density, ρ , of oligomeric dimethyl siloxane lubricating oil was measured in a range of $P = 0$ to 770 MPa and $T = 273$ to 419 K (29). The plot of the ambient pressure density versus temperature permitted calculation of: $Z_0 = -0.1924$, $Z_1 = 2.416 \times 10^5$ with the correlation coefficient squared, $r^2 = 0.9986$. From these values: $T^* = 9967$ K and $V^* = 9.162 \times 10^{-4}$ (m³/kg) were found. Next, from the actual ρ - T - P data, 51 values of P^* were computed. These values are presented in Fig. 1 as P^* versus P at $T = \text{const}$. The arithmetic average: $P_{av}^* = 644.4 \pm 38.3$ MPa was taken for the subsequent computation of $Y_s(\tilde{P}, \tilde{T})$.

The empirical values of η as reported in (29) are plotted in Fig. 2 versus the computed crowding (or packing) parameter $Y_s = 1/f$. It is worth noting that

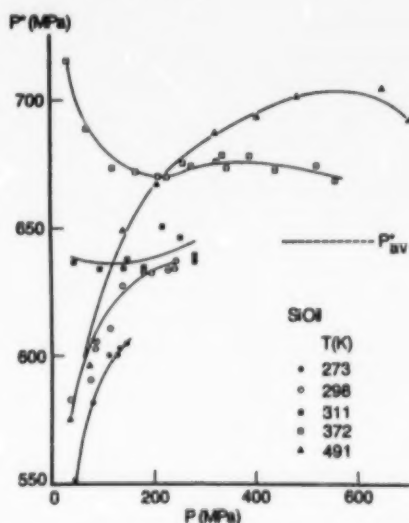


Fig. 1. Computed P^* versus P at the T indicated; the average value, P_{av}^* , is also marked. SiOil (29).

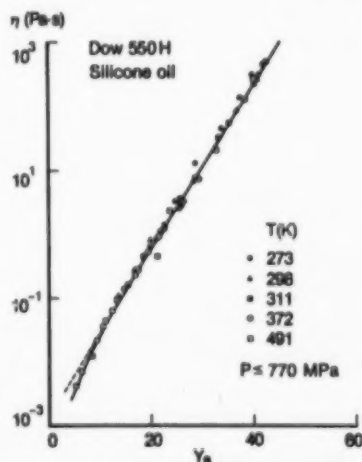


Fig. 2. Viscosity of SiOil versus Y_s at $T = 273$ to 491 K and $P \leq 770$ MPa (20).

for SiOil, using Eq 4, where Y_s replaced Y_D , a good description of η - P - T behavior is obtained. Here, in the range of $6.5 < Y_s < 42$, or η spanning five decades, $\log \eta$ is a linear function of Y_s .

Such a good superposition of data is unexpected in view of the uncertainty in determining P^* (see Fig. 1). It seems that the main sources of P^* -variability are the experimental errors and/or the approximations used during the computation procedure of F^* 's as introduced by use of Eqs 5 and 15. Both the P - V - T relation computed from Eqs 12 and 13 and the superposition of $\eta(P, T) = f(Y_s)$ demonstrate the soundness of the basic thermodynamic theory.

PDMS

The viscosities and specific volumes for commercial poly(dimethyl siloxane) (PDMS) were reported by Tokiura, *et al.* (30). The sample with the viscosity

average molecular weight, $M_c = 234,000$ was measured at $T = 298$ to 353 (K) and $P = 0$ to 100 MPa. The plot $\ln V$ versus $T^{3/2}$ is shown in Fig. 3. The least-squares fit to $P = 0$ data gives: $Z_0 = -0.15074$ and $Z_1 = 3.4797 \times 10^5$ with $r^2 = 0.9996$ from which $T^* = 7770$ K and $V^* = 9.537 \times 10^{-4}$ (m^3/kg) were calculated. The plot of P^* versus P at $T = \text{const.}$ is shown in Fig. 4. The average value $P^* = 439 \pm 18$ was computed. The plot of $\ln \eta$ versus Y_s is shown in Fig. 5. It is apparent that instead of one master curve there are clearly four isothermal dependencies i.e. apparently the unique correlation between η and f does not exist for this system. The maximum spread of η at $Y_s = \text{constant}$ is about 30 percent. While this is not a large error for melt viscosity data (see DISCUSSION), the systematic variability would be difficult to explain by inaccuracies in the measurements. It seems that the reason for lack of superposition comes not from η but Y_s .

It is worth noting that to calculate $Y_s(\tilde{T}, \tilde{P}) = Y_s(\tilde{T}, \tilde{V})$ the knowledge of the average P^* is not necessary; once $\tilde{T}$ and $\tilde{V}$ are known, Y_s can be found. Such a treatment is equivalent to assuming an individual value of P_i^* for each data point. For PDMS, this alternative method did not significantly improve the superposition. One has to conclude that for polymer melts the thermodynamic f is not nec-

essarily identical to the rheological one. The simplest way to incorporate this concept is by allowing the rheological scaling pressure $P_r^* \neq P^*$. As can be seen in Fig. 6, $P_r^* = 2P^*$ was required to generate a good superposition of the high viscosity data. However, in this case on superposition was obtained for low- η values.

It seems that PDMS exists in two different liquid forms: a low viscosity one for which the thermodynamic P^* provides a good master curve, and a high viscosity one for which $P_r^* = 2P^*$ is required to obtain superposition. The transition between them is defined by: T_{cr} , P_{cr} , plotted in Fig. 7.

The well-known Tait relation (31) can be cast into a reduced parameter form (32):

$$1 - \hat{V}(\hat{P}, \hat{T})/\hat{V}(0, \hat{T}) = C \ln [1 + \hat{P}/\hat{B}(\hat{T})] \quad (16)$$

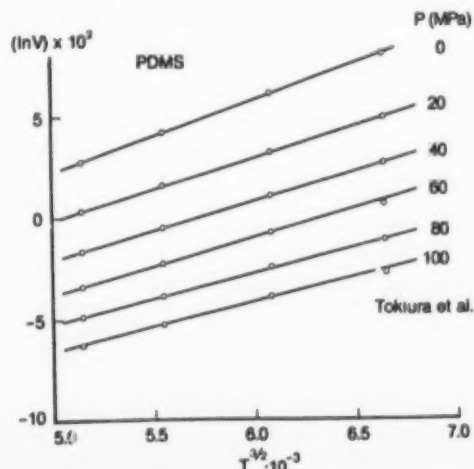


Fig. 3. Isobaric plot of the experimental V - T data for PDMS (30) according to Eq 14; $T = 298$ - 353 K and $P \leq 100$ MPa.

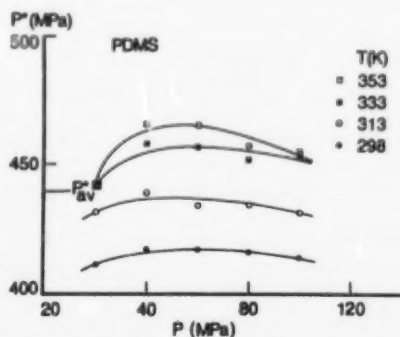


Fig. 4. Computed P^* versus P at the T indicated; average value, P_{av}^* , is marked. PDMS (30).

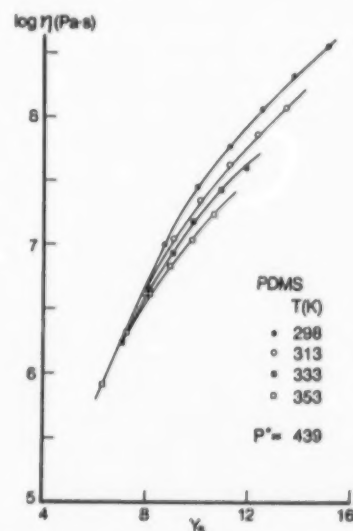


Fig. 5. η - Y_s relation for PDMS at the T indicated and $P \leq 100$ MPa (30). Y_s computed assuming $P_r^* = P^*$.

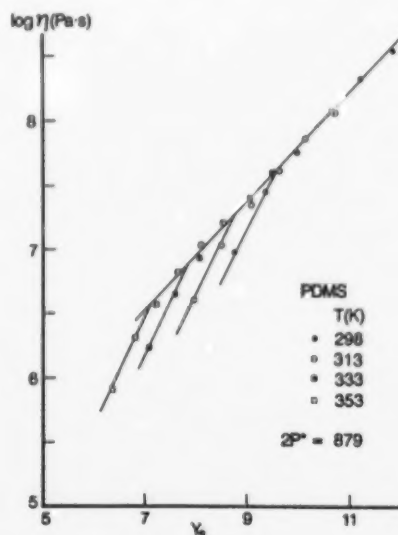


Fig. 6. The same data as in Fig. 5; here $P_r^* = 2P^*$ was assumed.

where the "universal constant", $C = 0.0894$ and B is the "Tait parameter" which depends only on T :

$$\hat{B}(\hat{T}) = B(T)/P^* \quad (17)$$

B can be directly computed from the coupled Eqs 12 and 13 using Eq 16 as the definition. Calculated in this manner $\hat{B}$ decreases with $\hat{P}$ by about 4 percent (Table 1).

Using the average values of $\hat{B}$, P^* can be calculated from Eq 17; these values are also listed in Table 1. It can be seen that there is a large difference between $P^* = 439 \pm 18$ calculated directly from P - V - T data and $P^* = 556 \pm 17$ calculated from the Tait parameter. When the latter value is used to compute Y_s , the resulting Fig. 8 shows a better clustering of data-points around a common dependence, but close scrutiny reveals a systematic tendency noted in Figs. 5 and 6. Discussion on the subject will continue after PB-Oils behavior is analyzed (next chapter).

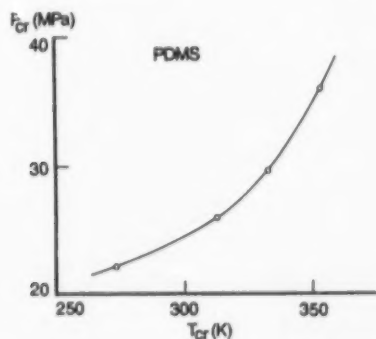


Fig. 7. The critical parameters P_{cr} versus T_{cr} for PDMS, as determined by intersection of the straight line dependencies $\ln \eta$ versus Y_s in Figs. 5 and 6.

Table 1. Computed Values of B for PDMS at $P = 0$ –100 MPa.

No	$T(K)$	$\hat{B}$ (range)	$\hat{B}$ (average)	B (Ref. 30)	P^* (MPa)
1	298	0.149–0.145	0.147	78.97	537
2	313	0.137–0.132	0.135	73.82	548
3	333	0.123–0.117	0.120	67.47	562
4	353	0.110–0.103	0.107	61.67	577
					P^* (average) = 556

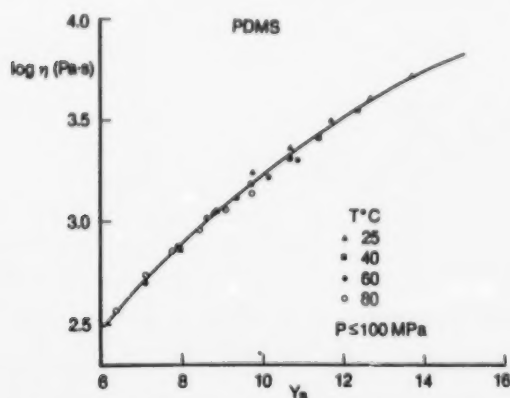


Fig. 8. $\ln \eta$ versus Y_s for PDMS (30); P^* used in calculation of Y_s was obtained from the Tait parameter B .

PB-Oils

Three poly(butylene) oils were examined (29). The samples, labeled here: PB-1, PB-2, and PB-3 (in order of increasing molecular weight, MW) were low MW lubricating oils. The reported MW = 645 ± 10 of PB-3 suggests the formula: $C_{46}H_{94}$. Both η and ρ were measured at $T = 273$ to 491 (K) and $P = 0$ to 1000 (MPa).

First, the P - V - T dependencies were examined. As before, V^* and T^* were computed (see Table 2) then P^* 's calculated from each individual P - V - T data point. An example of P^* versus P at $T = \text{const.}$ is shown in Fig. 9. The average values are listed in Table 2. In spite of variability of P^* the adequacy of Eqs 12 and 13 to describe the P - V - T dependence is excellent. The theoretical curves are well within the range of experimental accuracy for all three samples in the full range of variables. An example of $\hat{V}$ versus $\hat{P}$ at $\hat{T} = \text{const.}$ is shown in Fig. 10.

Next the ambient pressure viscosity was analyzed

Table 2. Scaling Parameters for PB-Oils.

Sample	$V^* \cdot 10^3$ (m ³ /kg)	T^* (K)	P^* (MPa)
PB-1	1.145	9019	767
PB-2	1.136	9049	713 ± 40
PB-3	1.132	9306	767

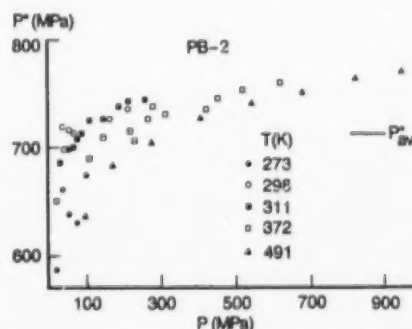


Fig. 9. Computed P^* versus P at the T indicated for PB-2; average value, P_{av}^* , is also marked (29).

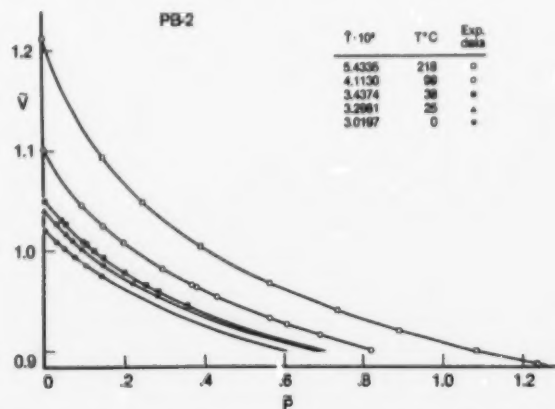


Fig. 10. Experimental (points) and computed from Eqs 12, 13 $\hat{V} - \hat{P}$ at $\hat{T} = \text{const}$ for PB-2 (29); for clarity most of the points at lower $\hat{V}$ were omitted.

using Eq 7. The results are presented in Fig. 11; good linearization with a reasonable value of the shielding parameter, $h = 0.887$, was obtained.

The pressure dependence of η is illustrated in Fig. 12 as $\log \eta$ versus P for PB-2 and Fig. 13 as $\log \eta$ versus ρ for PB-1. Finally, in Figs. 14 to 16, the dependence $\log \eta$ versus Y , is shown. In Fig. 12, the η smoothly increases with P ; this indicates absence of random experimental errors. The data in Fig. 13 is less consistent, suggesting that ρ -measurements may not be as precise. However, the plots in Figs. 14 to 16 show a lack of superposition. This behavior, similar to that observed for PDMS, cannot be explained either by experimental error or the P^* variability. The spread of η 's for PB-oils at $Y_1 =$

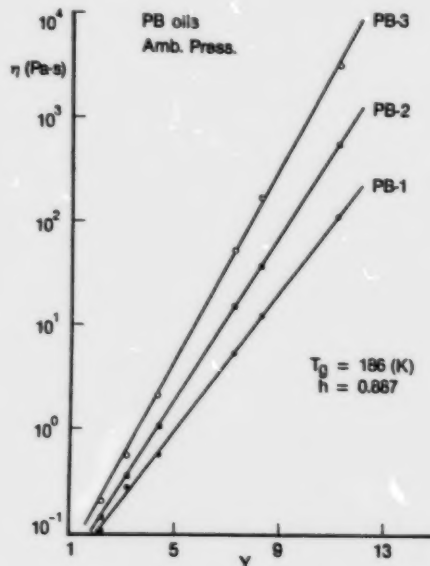


Fig. 11. Linearization of ambient pressure η - T dependence for PB (29) by means of Eq 7.

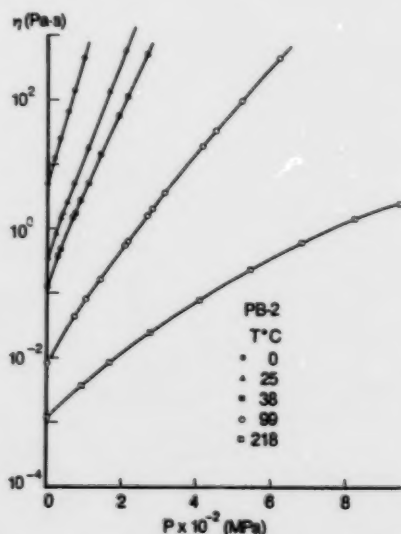


Fig. 12. Experimental isothermal η - P dependencies for PB-2 at the T indicated (29).

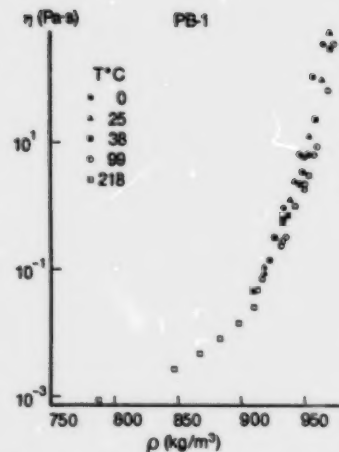


Fig. 13. Experimental plot of viscosity versus density, $\rho = \rho(P, T)$, for PB-1 (29); $T = 273$ - 491 K, $P \leq 1$ GPa.

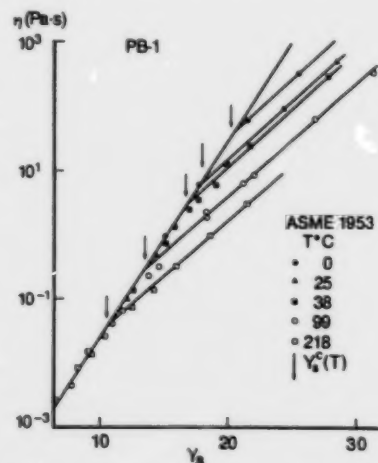


Fig. 14. $\eta - Y_8$ dependence for PB-1 (29); $P_{e^*} = P^*$ was assumed.

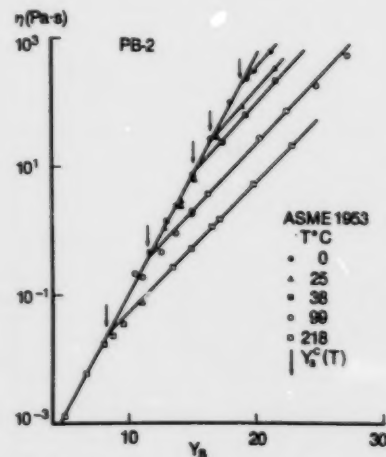


Fig. 15. $\eta - Y_8$ dependence for PB-2 (29); $P_{e^*} = P^*$ was assumed.

const. is much larger—a factor of about 22 is involved.

The arrows in Figs. 14 to 16 indicate the "transition" in flow behavior. The values of $P_{cr} = P_T$ at

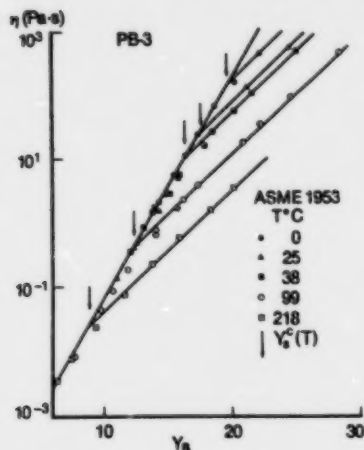


Fig. 16. $\eta - Y_g$ dependence for PB-3 (29); $P_r^* = P^*$ was assumed.

which the break occurs at each T are presented in Fig. 17. The dependence is linear, extrapolating to a common point: $T_T = 216(K)$ at $P = 0$. Should the behavior observed in Figs. 14 to 16 be due to a transition, then this would be observed at ambient pressure at T_T . The glass transition temperature, $T_g = 189(K)$ can be calculated from $T_g(MW \rightarrow \infty) = 249(K)$ (33) and the empirical dependence (34):

$$T_g = T_g(\infty) - 3.87 \cdot 10^4 / MW. \quad (18)$$

The ratio of $T_T/T_g = 1.14$ is within the limit of the ratio of the liquid-liquid to glass transition temperatures: $R_{LL} = T_{LL}/T_g = 1.13$ for polypropylene to 1.19 for polyhexene (35). Furthermore, from the relation (36):

$$D_1 = dT_{LL}/dP(\text{MPa}) = 280/T_g - 0.2 \quad (19)$$

$D_1 = 1.28$, to be compared with the experimental value (Fig. 17) of 1.18 ± 0.01 . This is a reasonable agreement considering the experimental uncertainty and the approximate nature of Eqs 18 and 19. In short, T_T can be identified with the T_{LL} transition temperature.

It is worth-recalling that the discontinuity in $\eta - T$ and $\eta - c$ have been previously reported for a number of liquids (7 to 10). The discontinuity in $\eta - P$ is not an oddity but a natural consequence of the existence of different liquid structures.

The break in $\ln \eta$ versus Y_g for PDMS was also noted. However, judging by the data in Fig. 7 the transition under ambient pressure should be observed at $T < 250 K$. If indeed the observed transition is of the liquid-liquid type, then this should not be a surprise; $T_g = 146 K$ for PDMS and if $R_{LL} = 1.1$ to 1.2, then $T_{LL} \approx 160$ to 175 K is to be expected.

PP

Hercules Pro-fax 6523 propylene (PP) was investigated at $T = 487$ to 506 (K) and at $P = 0$ to 138 (MPa) (37). Because of the limited range of variables, the F^* 's were taken from Zoller (38): $P^* = 542$ (MPa), $T^* = 11155$ (K), and $V^* = 1.195 \cdot 10^{-3}$ (m^3/kg). The $\eta - Y_g$ dependence is shown in Fig. 18.

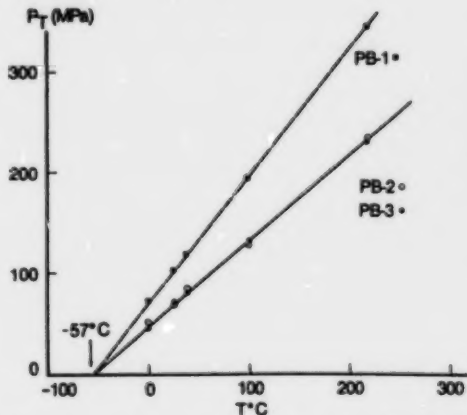


Fig. 17. The critical parameters $P_T = P_c$ versus $T_T = T_c$ for PB as determined by intersects of the straight lines $\ln \eta$ versus Y_g in Figs. 14 to 16.

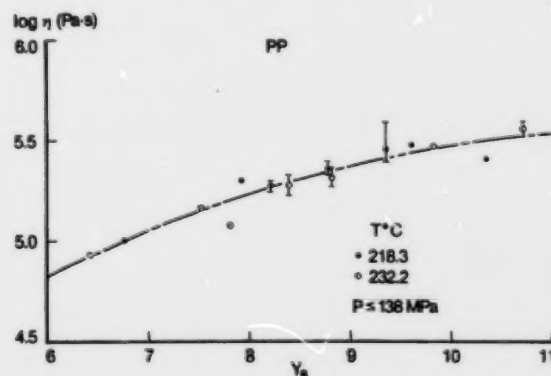


Fig. 18. $\eta - Y_g$ dependence for PP at $T = 487$ and 506 K and $P \leq 138$ MPa (37); $P_r^* = P^*$ was assumed.

Since the authors provided η -values for repetitive runs, the bars indicate the experimental spread of data. There is no systematic variation between the two isothermal sets. It is apparent that within the experimental error the results follow a "master curve".

For PP (35): $T_g = 264.5$, $T_{LL} = 298$ and $P = 0$ and its value at $P = 138$ (MPa) can be calculated from Eq 17 as $T_{LL} = 416$ (K). This indicates that the η -measurements were carried out at $T < T_{LL}$, within a single liquid structure. Because of limited range of T and a large scatter of data the calculations were not repeated for $P_r^* = 2 P^*$.

LDPE

The data on low density polyethylene (LDPE) were reported by Cogswell, *et al.* (39), Karl (40), and Christmann, *et al.* (41, 42). These will be discussed separately.

- Cogswell and McGowan (39) reported η at $T = 423$ to 543 (K) and $P = 0$ to 175 MPa. To compute Y_g , the F^* 's were taken from (32): $P^* = 729$ (MPa), $V^* = 1.167 \times 10^{-3}$ (m^3/kg), and $T^* = 10620$ (K). The results are presented in the lower part of Fig. 19; in the upper part of the same data are plotted versus Y_g , computed, assuming $P_r^* = 2 P^*$.

The latter plot indicates better superposition.

- Karl (40) measured one sample at $T = 403, 428$, and 463 (K) and $P = 0$ to 500 MPa. In the capillary flow shear crystallization was observed at the two lower temperatures. Since the density, ρ , versus P data were not measured the F^* 's were taken from (32). The results of computations are presented in Fig. 20.
- Christmann, *et al.* (41, 42), using four different rheometers measured two series of PE's: I with the $M_n \approx 12,000$ and variable M_w/M_n , and II with $M_w/M_n \approx 6$ and variable M_w (Table 3). The η -data were determined at $T = 413$ to 493 (K) and $P = 5$ to 50 (MPa). Excepting the two commercial resins, Lupolen and Hostalen, the other samples were special products. Lupolen is LDPE, Hostalen with $\rho = 947$ kg/m³ high density polyethylene, HDPE, the others of unknown type. The plot of η versus M_w (Fig. 21) permits the expression:

$$\eta = 2.12 \times 10^{-13} M_w^{3.35}, \quad r^2 = 0.950 \quad (20)$$

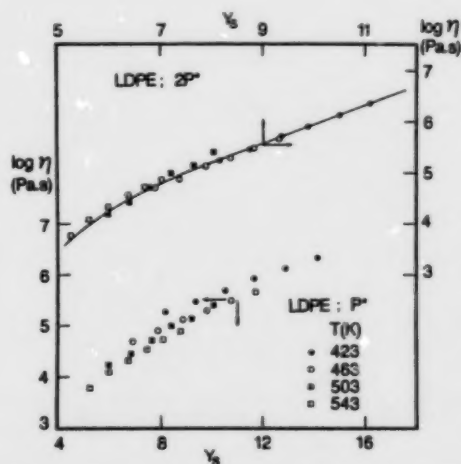


Fig. 19. $\eta - Y_c$ dependence for LDPE (39) at $T = 423$ to 543 K and $P \leq 175$ MPa; for the lower set of points $P_r = P^*$ and for the upper $P_r = 2P^*$ were assumed.

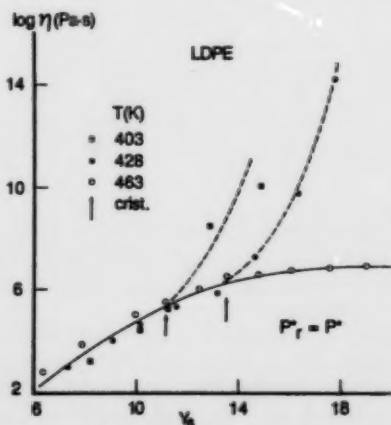


Fig. 20. $\eta - Y_c$ dependence for LDPE (40) at $T = 403$ to 463 K and $P \leq 500$ MPa; $P_r = P^*$ was assumed. The arrows indicate onset of crystallization at the two lower temperatures.

Table 3. Characteristics of PE Samples (41, 42).

Series	N ^a	M _n · 10 ⁻³	M _w · 10 ⁻³	M _w /M _n	Type
I	1	14	52	3.7	Hostalen GD6250, HDPE
	2	12	62	5.2	
	3	12	69	5.8	
	4	9.8	73	7.4	
	5	22	210	9.6	
	6	12	100	~11.0	
	7	12	150	12.5	Lupolen 6011D, LDPE
	8	15	220	14.6	
	9	12	280	~21.0	
II	1		36.6	5 to 6	
	2		81.5	"	
	3		103	"	
	4		138	"	
	5		197	"	
	6		223	"	

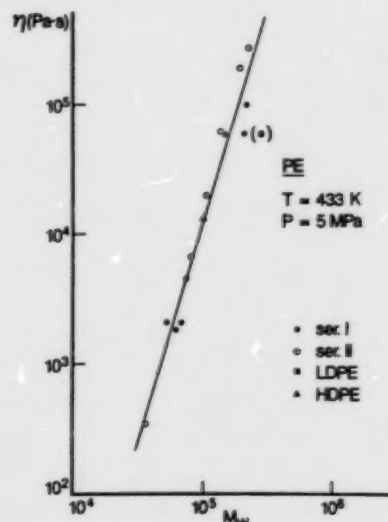


Fig. 21. $\eta - M_w$ correlation for various polyethylenes (see text) at $T = 433$ K and $P = 5$ MPa (41, 42). The line represents Eq 18.

for all but the Lupolen samples. On this basis, it seems reasonable to assume that most of the tested PE's were of the HDPE-type. These will be discussed later.

In Fig. 22, η versus Y_c is shown for sample I/9. Here, to calculate Y_c , the F^* 's were taken from (32). Both $P_r = P^*$ and $P_r = 2P^*$ were used. The fit in both cases is good, although the second order curve fit in the first case is better ($r^2 = 0.996$) than in the second ($r^2 = 0.987$).

HDPE

Here, two sources of η - P - T data are available; those of Cogswell and McGowan (39) and of Christmann and Knappe (41, 42). For both sets the F^* 's were taken from (32). In both cases the two assumptions, $P_r = P^*$ and $P_r = 2P^*$, were examined. The results presented in Figs. 23 to 25 are those obtained for the second case.

As can be seen in Fig. 23, the low temperature data (39) show significant deviations; the other viscosities seem to follow Y_c quite well.

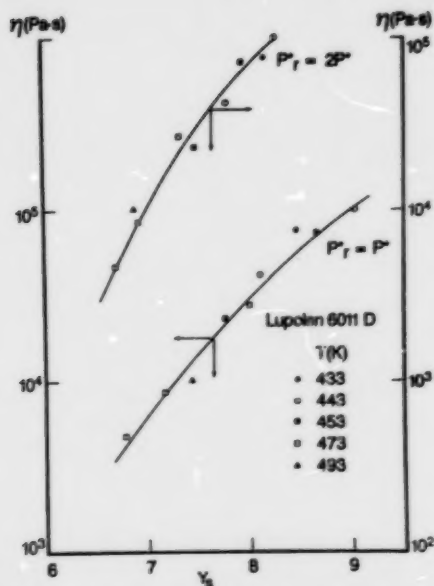


Fig. 22. $\eta - \dot{\gamma}_s$ for Lupolen 6011 D (41, 42) at $T = 433$ to 493 K and $P \leq 50$ MPa; both values $P_r^* = P^*$ (lower set) and $P_r^* = 2P^*$ (upper set) were assumed. The lines represent second order polynomials.

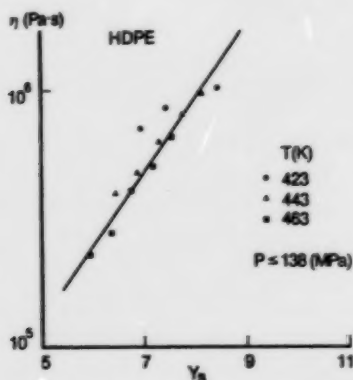


Fig. 23. $\eta - \dot{\gamma}_s$ for HDPE (39) at $T = 423$ to 463 K and $P \leq 138$ MPa; $P_r^* = 2P^*$ was assumed.

In Figs. 24 and 25, the data for the two series of PE's (41, 42) are presented. In both cases, a good fit to a single master curve is found. For PE I, the data for constant M_n and variable M_w/M_n are presented in Fig. 24. As the polydispersity increases the slope

$$D_2 = d \ln \eta / d \dot{\gamma}_s \quad (21)$$

decreases. An exception is sample I/7, with a much steeper increase than expected on the basis of its $M_w/M_n = 12.5$. For PE II, where M_w/M_n remains constant and M_w changes, the data in Fig. 25 for the three lowest M_w samples follow the "master curve", but those of $M_w \geq 138,000$ show poor overlapping. The experimental values, as reported by the authors, change little with P ; e.g. at 453 K and P varying from 5 to 20 , 35 and 50 MPa $\eta \times 10^5$ (Pa.s) varies: from 1.2 to 1.2 , 1.3 and 1.3 , respectively. i.e. is nearly constant within the range of experi-

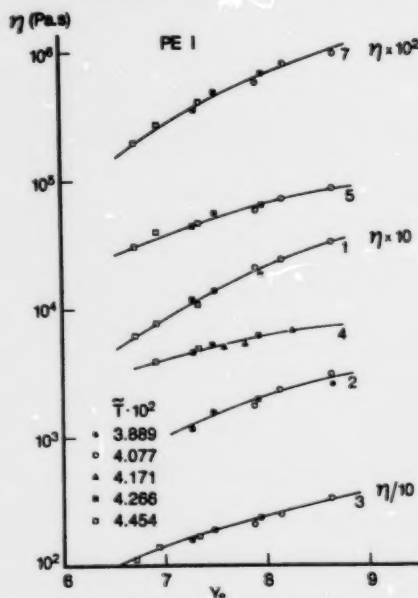


Fig. 24. $\eta - \dot{\gamma}_s$ dependence for the first series of polyethylenes (41, 42) in which M_n was relatively constant and polydispersity changed (Table 3); $T = 423$ to 493 K and $P \leq 50$ MPa. $P_r^* = 2P^*$ was assumed.

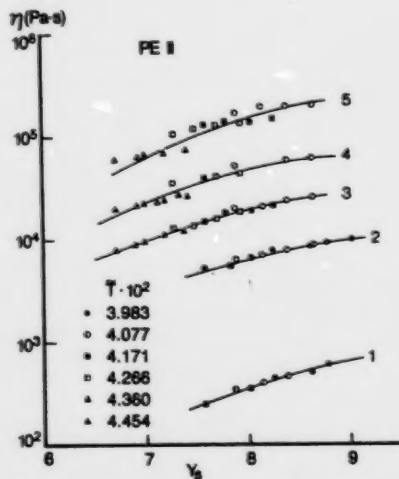


Fig. 25. $\eta - \dot{\gamma}_s$ dependence for the second series of polyethylenes (41, 42) in which polydispersity was nearly constant ($M_w/M_n = 5$ to 6) and M_w varied; $T = 413$ to 493 , $P \leq 50$ MPa and $P_r^* = 2P^*$.

mental errors. Considering the other data on $\eta - P$ dependence of HDPE presented in Figs. 23 and 24, it seems that this is an artifact of either the measurement method or the extrapolation of data to zero rate of shear. It is worth noting that for PE II, the slope D_2 is nearly constant and its value in agreement with those in Fig. 24. This may be a significant impact on the generalization of this approach. If the curves $\eta - \dot{\gamma}_s$ for samples of similar polydispersity have a similar form, then they can be scaled up by vertical shifting in a manner previously proposed (12) for n -paraffins. As a corollary, samples of different polydispersity (and branching) cannot be scaled by simple vertical shifting.

PS

The data on the T and P dependence of η for polystyrene (PS) were tabulated by Cogswell and McGowan (39). To calculate Y_s , the values of F^* 's were taken from the Olabisi and Simha paper (32). The assumption $P_r^* = 2 P^*$ was used. The results are shown in Fig. 26. In the full range of $T = 443$ to 483 (K) and $P = 0$ to 140 (MPa), in which η varies within four decades, the data follow a single "master curve". In the figure, the data of Knappe, *et al.* (43) at $T = 438$ (K) and $P = 0$ to 145 (MPa) are also shown as open squares. Except the lowest η -value (ambient P), all the other points follow the results reported by Cogswell and McGowan.

PMMA

Viscosities of poly(methyl methacrylate), PMMA, at $T = 493$ to 523 (K) and P up to 173 (MPa) were reported by Cogswell and McGowan (39) and those at $T = 413$ to 528 and $P = 5$ to 50 (MPa) by Christmann, *et al.* (41, 42). To compute Y_s , the F^* 's were taken from Olabisi and Simha (32). The resulting plots η versus Y_s for $P_r^* = 2 P^*$ are presented in Fig. 27.

Data from both sources are presented in the figure. For each polymer, all the results of isothermal η - P measurements followed the same "master curve". To avoid confusion there is no distinction of temperature in the figure. In spite of overlapping ranges of Y_s for the two sources of data, those from Cogswell follow a distinct curvature, similar to the one observed for n -paraffins, while the ones from Christmann give straight lines. The parameters of these lines

$$\eta = A_2 \exp \{B_2 Y_s\} \quad (22)$$

with the correlation coefficient squares are listed in Table 4 along with the molecular parameters (41, 42) and $\eta(Y_s = \text{constant})$.

There is no correlation between the slope B_2 and M_w/M_n . In fact, assuming the average value of B_2 for all samples: $B_3 = 2.33 \pm 0.15$, the appropriate values of A_3 listed in Table 4 can be calculated from Eq. 22. It can be seen that again there is no correlation between the molecular parameters M_w or M_w/M_n and A_2 , A_3 , or $\eta(Y_s = \text{const.})$. In particular, η 's of

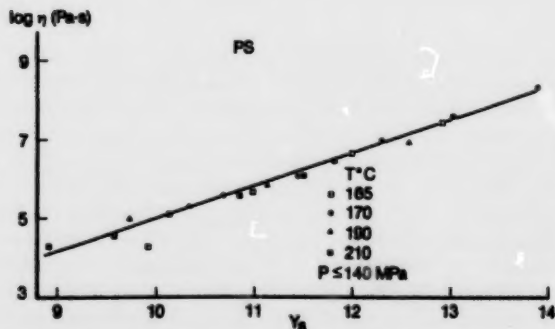


Fig. 26. $\eta - Y_s$ dependence for PS from (39) at $T = 443$ to 483 K and $P \leq 140$ MPa and from (43) at $T = 438$ K and $P \leq 145$ MPa; $P_r^* = 2P^*$ was assumed.

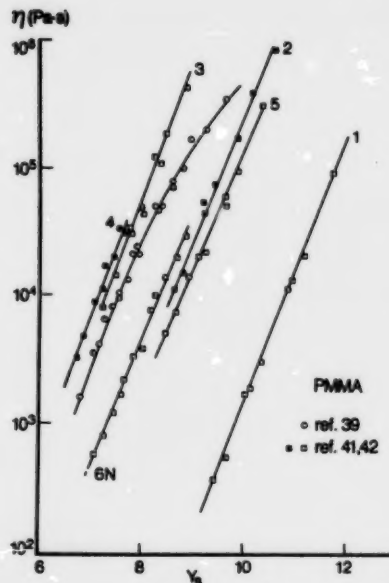


Fig. 27. $\eta - Y_s$ dependence for PMMA at $T = 493$ to 523 K and $P \leq 173$ MPa for one sample (39) and $T = 413$ to 528 K and $P \leq 50$ MPa for the others (41, 42). Since there were no systematic differences between different isothermal sets of data, there is no distinction of T in the figure; the two types of points were only used to distinguish dependencies of different samples.

sample 5 seems to be about an order of magnitude too small. The origin of this discrepancy is unknown.

DISCUSSION

In Table 5 the systems analyzed in this work are listed, along with their F^* 's values. Out of the eight systems, two followed those previously observed for n -paraffins behavior with $P_r^* = P^*$ (SiOil, PP), two demonstrated a transitional behavior (PDMS, PB), in one case (LDPE) depending on the source of data, the results could be fitted either with $P_r^* = P^*$ or $P_r^* = 2P^*$, and the remaining three systems (HDPE, PMMA, and PS) obeyed the $P_r^* = 2P^*$ assumption.

The error in rheological testing under ambient pressure depends on the type of equipment and care during the measurements. Under the best circumstances ± 5 percent accuracy is obtained, while in capillary flows ± 20 percent is considered reasonable. In the high pressure measurements a spread of data up to 70 percent was reported (42).

Other sources of error are the methods of extracting the zero-shear viscosities from the measured shear rate dependent function, $\eta_{\dot{\gamma}}$. In most of the source references the method is not provided. In the case of LDPE, HDPE, and PMMA (41, 42) the Spencer-Dillon (44) principle:

$$1/\eta = \lim_{\sigma_{12} \rightarrow 0} \eta_{\dot{\gamma}}^{-1} \quad (23)$$

was used (σ_{12} is the shear stress). However, this principle was shown (45) to lead to significant error; the Newtonian viscosity is reached at final (but undefined) value of $\sigma_{12,c} \neq 0$. This means that the quoted (41, 42) η 's are most likely too high. It is

Table 4. Characteristics of PMMA Samples (41, 42).

N°	$M_w \cdot 10^{-3}$	M_w/M_n	$A_2 \cdot 10^5$	B_2	r^2	$A_3 \cdot 10^2$	$\eta(\gamma_s = 8.5) \times 10^{-4}$
1	13	1.73	0.005455	2.392	0.995	0.01081	0.0039
2	48	1.78	3.0947	2.291	0.979	2.174	2.7
3	105	1.95	9.0829	2.526	0.990	44.318	21.
4	160	2.35	64.1404	2.311	0.967	56.476	26.
5	160	2.96	9.2616	2.111	0.989	1.168	1.6
6N	124	1.85	5.6734	2.277	0.993	3.758	1.4
6H	184	1.96	47.8334	2.169	0.977	13.555	7.6

Table 5. Summary of Results.

No.	System	Range of variables			Reducing Parameters				Superposition	
		T (K)	P (MPa)	Ref.	P* (MPa)	T* (K)	V* · 10 ³ (m ³ /Kg)	Ref.	P*/P*	depend.
1	SiOil	273-419	0-770	29	644.4	9967	0.916	this work	1	linear
2	PDMS	298-353	0-100	30	439	7770	0.954	"	1 & 2	trans.
3	PB-1	273-491	0-1000	29	767	9019	1.145	"	"	"
	PB-2	273-491	0-1000	29	713	9049	1.136	"	"	"
	PB-3	273-491	0-1000	29	767	9306	1.132	"	"	"
4	PP	487-506	0-138	37	542	11155	1.195	38	1	curve
5	LDPE	423-543	0-175	39	729	10620	1.167	32	2	"
	"	403-463	5-500	40	729	10620	1.167	"	1 or 2	"
	"	413-493	5-50	41, 42	729	10620	1.167	"	1 or 2	"
6	HDPE	423-463	0-140	39	716	10046	1.155	"	2	linear?
	"	413-493	5-50	41, 42	716	10046	1.155	"	2	curves
7	PS	443-483	0-140	39	745	12680	0.960	"	2	linear?
8	PMMA	493-523	0-173	39	930	11890	0.835	"	2	curve
	"	413-528	5-50	41, 42	930	11890	0.835	"	2	linear

easy to see that according to Eq 23 η is defined as the true zero-shear stress (or shear rate) parameter, whereas for most systems the Newtonian plateau: $\sigma_{12} \propto \dot{\gamma}$ is found for $\sigma_{12} \leq \sigma_{12,c}$.

Another possible source of error is the computational procedure of F^{**} s. It is based on the assumption that Eq 5 is a good approximation of the $\dot{V} - \dot{T}$ behavior, as predicted by the coupled Eqs 12 and 13. While Eq 5 can reproduce the exact value of V given by Eqs 12 and 13 to a fraction of a percent, nevertheless it is an approximation of a higher order curve. As a consequence particularly V^* , determined from extrapolation of $\dot{V} - \dot{T}$ and $V - T$ to $T = 0$, is sensitive to the selected zone of $\dot{T}$ used to compute S_0 (viz. Eq 15). The changes in V^* are further magnified in calculating Y_0 . Obviously, one should bypass Eq 5 simultaneously computing F^{**} s from fitting experimental data directly to Eqs 12 and 13. This procedure is being developed at DSM in Holland (46). The variability of P^* presented in Figs. 4 and 9 is, at least partially, due to imprecise determination of V^* and T^* .

The difficulties in determination of η as well as those in computation of F^{**} s do not explain why it is that for most polymers the rheological P_r^* is about twice as large as P^* . It should be mentioned that from superposition of the pressure dependent dynamic data for four rubbers Moonan and Tschoegl (47) found $P_r^*/P^* = 1.29$ to 2.23.

In PS, PMMA, and HDPE, where $P_r^* = 2P^*$, there is either "more" free volume available for flow or there is a "more economical" way to utilize the available volume. The theory predicts that (28):

$$P^*V^*/T^* = R/3M_0 \quad (24)$$

where R is the gas constant and M_0 is the molecular weight of the statistical segment defined as: $M = sM_0$, where M is the molecular weight of the polymeric molecule. Increasing P^* by a factor of two indicates that in flow, the effective segment length is about one-half of that observed in thermodynamics. From the first table of (32), one can write:

$$M_0 = 4.6868 \cdot 10^{-3} T^* - 12.5876; \quad (25)$$

$$r^2 = 0.948,$$

i.e. thermodynamically the lattice cell volume (proportional to M_0) increases linearly with T^* , at T^* varying from 5880 to 12740 K. Alternatively the data for n -paraffins (25, 26) can be presented as:

$$M_0 = 33.278/[1 + 6.5265/n]; \quad (26)$$

$$r^2 = 0.9979,$$

where n is the number of carbon atoms in n -paraffin chain. For $n \rightarrow \infty$, i.e. for HDPE, $M_0 = 33.278$ to be compared with the experimental values: 31.7 to 33.7. In short, the P - V - T results indicate a systematic increase of cell volume with the size of the molecule.

It is interesting to note that the requirement: $P_r^* = 2P^*$ is equivalent to reduction of cell volume by a factor of two, i.e. reduction of M_0 to about 16-17, characteristic of C_6 to C_7 . If the flow occurs by coordinated segmental jumps, one may expect that in a homologous series the size of the segment (for molecules above a certain size) will be relatively independent of the total molecular weight. It seems that the analysis provided in this paper indicates this to be the case.

In some systems (PDMS, PB) a transition has been observed. The pressure at which the transition occurs increased with T . The plot of these $P_{cr} - T_{cr}$ pairs is a sort of phase diagram for transition in flow, equivalent to a standard $V - T$ diagram. In the area of higher T and lower P (or higher V) $P_r^* = P^*$ is obeyed, on the other side of the curve $P_r^* = 2P^*$. It should be noted that the factor of 2 is not the optimal value required for superposition of $\eta - Y_c$ data on a single curve; in this work, the factor was chosen arbitrarily to facilitate the procedure. This is justified only by previous computation of data (15) in which 2.0 ± 0.2 was found for PS and PMMA.

In Fig. 21 η versus M_w plot is shown for PE's. The data follow relatively well ($r^2 = 0.950$) Eq 20. Since the extrapolation method to obtain the Newtonian η is suspect, the relation should be compared with other reported results. The recent data (48):

$$\eta_0 = 2.692 \cdot 10^{-14} M_w^{3.49}; \quad r^2 = 0.996 \quad (27)$$

compared fairly well with Eq 20. As expected, Cristmann's data are higher by a factor of 1.8 at the lower, and by 1.4 at the higher end of the M_w range. This relatively constant variation may be due to the pressure effect ($P = 5$ MPa data were used) and it should not influence the validity of conclusions drawn from $\eta - Y_c$ dependencies for these resins.

CONCLUSIONS

The zero-shear viscosity of liquids can be written as a unique function of the free volume, f :

$$\ln \eta = A_4 + A_5/(f + A_6) \quad (28)$$

where A_i are parameters and f is the effective free volume: $f = f(T/T^*, P/P_r^*)$. For low-viscosity liquids: $P_r^* = P^*$, for high- η ones: $P_r^* = 2P^*$. To calculate $\eta(P)$ at $T = \text{const.}$ one should determine $\eta = \eta(T)$ in as wide a range of T as possible. Using $P_r^* = 2P^*$ such a dependence can be cast into a form of Eq 28 in which f is accessible from statistical thermodynamics.

The above recommendation is valid within the full range of independent variables only for liquids of the same structure. In systems undergoing phase transition (crystallization or liquid-liquid type) the treatment has to be different for each phase; usually superposition of the lower- η phase can be accomplished using $P_r^* = P^*$, whereas that of the higher- η one using $P_r^* = 2P^*$.

It is highly advisable to develop a simultaneous fit of P - V - T data to Eqs 12 and 13. Such a method, bypassing the empirical Eq 5, will lead to improved precision in determination of F^* 's. This improvement is needed to achieve desired accuracy in computation of f .

Finally, the need for $\eta(P, T)$ data for polymeric liquids must be stressed. Even within the low pressure range observed during extrusion, $P < 50$ MPa, these are difficult. The data in the higher range, $P < 700$ MPa, experienced in injection molding, are virtually nonexistent (see Table 5). The analysis of $\eta(P, T)$ data of oligomeric and polymeric liquids

demonstrates the complexity of the problem. The complexity is a consequence and extension of the behavior observed previously under the ambient pressure (7 to 9). It would be unrealistic to expect $\eta = \eta(P)$ to be simpler than $\eta = \eta(T)$. In both cases the liquid-liquid or liquid-solid transitions have to be watched for. However, within a single phase (structure) the $\eta(P, T)$ dependence can be predicted.

One particularly interesting conclusion of this work is that in a homologous series of liquids, i.e. in a series of liquids with variable molecular weight (viz. n -paraffins, HDPE of constant polydispersity) it is possible to generate a master curve for the whole series. In this case Eq 28 can be expressed as:

$$\ln \eta/\eta^* = A_5(f^* - f)/(f + A_6)(f^* + A_6) \quad (29)$$

where η^* is the viscosity at an arbitrarily selected value of f^* . Equation 29 has a particularly simple form in cases where $A_6 = 0$, as for SiOil, HDPE, PS, and PMMA and for PDMS and PB at $P \geq P_{cr}$.

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NOMENCLATURE

$A_i, B_i; i = 0$ to 6	= Equation constants.
b	= Van der Waals constant.
$B(T)$	= Tait parameter.
$\tilde{B}(T)$	= reduced Tait parameter, Eq 17.
$C = 0.0894$	= Universal Tait constant.
D_1, D_2	= Derivatives defined by Eqs 19 and 21, respectively.
E_a	= Activation energy of flow, J/mol.
f	= Free volume fraction.
$F, F^*, \tilde{F}$	= Function, reducing parameter, and reduced function; $F = P, V, T$.
h	= Hydrodynamic shielding parameter of Eq 6.
i	= Number of computed $\tilde{P}\tilde{V}\tilde{T}$ point.
$K(T)$	= Cogswell proportionality factor, Eq 3.
M_0	= Molecular weight of the equivalent segment.
MW	= Macromolecular weight.
M_n, M_w, M_z	= Number, weight, and z -average molecular weights.
n	= Number of carbon atoms in a molecular chain.
P	= Pressure, Pa.
$P^*, \tilde{P}, P_K$, and P_{cr}	= Reducing, reduced, critical

- (see Eq 10) gas-liquid and critical (see Figs. 7, 17) liquid-liquid values of P , respectively.
- $P^{\circ}_{av}, P_r^{\circ}$ = Arithmetic average value of P° and its rheological equivalent.
- r^2 = Correlation coefficient squared.
- R_{LL} = T_{LL}/T_g .
- R = Gas, constant, 8.314/mole K.
- s = Number of equivalent segments per molecule.
- S_0, S_1 = Intercept and slope in Eq 5.
- T, T_g, T_m = Temperature, glass transition temperature, and melting temperature, K.
- $T^{\circ}, \hat{T}$ = Reducing and reduced T .
- $T_g(\infty)$ = T_g for $M_w \rightarrow \infty$.
- T_T = Transition T .
- T_K, T_{cr}, T_{LL} = Gas-liquid, Eq 10, critical and liquid-liquid values of T_T .
- V, V_0 = Volume, volume at 0(K), L/kg.
- $V^{\circ}, \hat{V}$ = Reducing and reduced V .
- $V_{o,eff}$ = Rheologically effective occupied volume.
- V_s = Crystalline volume.
- V_K = Critical (gas-liquid) volume.
- y = Occupied site fraction.
- Y_D, Y, Y_c = Variables defined by Eqs 4, 7, and as $1/(1 - y)$, respectively.
- Z_0, Z_1 = Intercept and slope of the experimental plot: $\ln V$ versus $T^{3/2}$, Eq 14.
- $\dot{\gamma}$ = Rate of shear (s^{-1}).
- δ = $\ln(\hat{V}_{i+1}/\hat{V}_i)$.
- Δ = Constant in Eq 11.
- η = Zero shear viscosity, Pa·s.
- ρ = Density, kg/L.
- σ_{12} = Shear stress (Pa).
- $\sigma_{12,c}$ = Maximum value of σ_{12} at which viscosity starts to decrease from η .
- ϕ = $1/(yV)$ variable in Eqs 12 and 13.
- Ω = Occupied volume, Eq 8.
- HDPE, LDPE = High and low density polyethylene, respectively.
- PB-1, PB-2, PB-3 = Poly(butene-1) samples 1, 2, and 3, respectively.
- PDMS = Poly(dimethyl siloxane).
- PMMA = Poly(methyl methacrylate).
- PP = Polypropylene.
- PS = Polystyrene.
- SiOil = Oligo(dimethyl siloxane).

REFERENCES

- NRCC-IMRI mini-symposium series on mathematical modeling of plastics processing and properties: "Modeling-82" held February 9th, 1982, published in *Polymer Eng. Sci.*, **22**, No. 17, (1982); "Modeling-83", held February, 1983, published in *Polymer Eng. Sci.*, **24**, No. 9, (1984).
- P. Avenas, J. F. Agassant, and J. Ph. Sergent, "La Mise en Forme des Matières Plastiques," T & D. Lavoisière, Paris, (1982).
- J. R. A. Pearson and S. M. Richardson, Eds., "Computational Analysis of Polymer Processing," Applied Science, London, (1983).
- F. N. Cogswell, "Polymer Melt Rheology," G. Godwin Ltd., London, (1981).
- A. B. Metzner in "Processing of Thermoplastics Materials," E. C. Bernhardt, Ed., R. E. Krieger Publ. Co., Malabar, FL, 1959, Section I.
- L. A. Utracki, *Polymer Eng. Sci.*, **23**, 446 (1983).
- L. A. Utracki, *J. Macromol. Sci., Phys.*, **B10**, 447 (1974).
- L. A. Utracki, *J. Macromol. Sci., Phys.*, **B18**, 731 (1980).
- L. A. Utracki and R. Simha, *J. Rheol.*, **25**, 329 (1981).
- L. A. Utracki, *Polymer Eng. Sci.*, **22**, 81 (1981).
- L. A. Utracki and R. Simha, *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.*, **23**, 67 (1982).
- L. A. Utracki, *Canad. J. Chem. Eng.*, **61**, 753 (1983).
- R. Simha and C. E. Weil, *J. Macromol. Sci.-Phys.*, **B4**, 215 (1970).
- A. J. Batschinski, *Z. Phys. Chem.*, **84**, 643 (1913).
- L. A. Utracki, *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.*, **24**, 113 (1983).
- R. Simha and T. Somcynski, *Macromolecules*, **2**, 342 (1969).
- J. E. McKinney and R. Simha, *Macromolecules*, **9**, 430 (1976).
- R. Simha, *Makromol. Chem. Suppl.*, **2**, 143 (1979).
- R. K. Jain and R. Simha, *J. Chem. Phys.*, **72**, 4909, (1980).
- R. K. Jain and R. Simha, *Macromolecules*, **13**, 1501 (1980).
- R. K. Jain, R. Simha, and P. Zoller, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1399 (1982).
- R. Simha, *Macromolecules*, **10**, 1025 (1977).
- R. K. Jain and R. Simha, *Berichte Bunsen Ges. Phys. Chem.*, **85**, 626 (1981).
- O. Olabisi and R. Simha, *Macromolecules*, **8**, 211 (1975).
- R. K. Jain and R. Simha, *J. Chem. Phys.*, **85**, 2182 (1981).
- R. K. Jain and R. Simha, *J. Chem. Phys.*, **70**, 5329 (1979).
- J. C. Curro, R. R. Lagasse, and R. Simha, Paper presented at Phoenix meeting of the A.P.S., March 16-18, 1981, see also *J. Appl. Phys.*, **52**, 5892 (1981); *Macromolecules*, **15**, 1621 (1982).
- R. Simha, *Polymer Eng. Sci.*, **22**, 74 (1982).
- American Society of Mechanical Engineers, "Viscosity and Density of over 40 Lubricating Fluids of Known Composition at Pressures to 150,000 PSI and Temperature to 425°F," Research Report on Pressure Viscosity, Vols I and II (1953).
- S. Tokiura, S. Ogihara, T. Takaki, and H. Sasaki, "Proceedings Intl. Congress Rheolog. Tokyo 1968," S. Onogi (Ed.), Tokyo Press pg. 275 (1970).
- P. G. Tait, in *Rept. Sci. Results Voyage H.M.S. Challenger*, *Phys. Chem.*, **2**, 1-76 (1888).
- O. Olabisi and R. Simha, *J. Appl. Phys.*, **21**, 149 (1977).
- W. A. Lee, *J. Polymer Sci.*, **A-2**, **8**, 555 (1970).
- R. F. Boyer, *Macromolecules*, **7**, 142 (1974).
- R. F. Boyer, *J. Macromol. Sci. Phys.*, **B18**, 455 (1980).
- R. F. Boyer, *Colloid Polym. Sci.*, **258**, 760 (1980).
- R. G. Foltz and K. K. Wang, *J. Non-Newt. Fluid Mech.*, **3**, 347 (1978).
- P. J. Zoller, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1491 (1978).
- F. N. Cogswell and J. C. McGowan, *Br. Polym. J.*, **4**, 183 (1972).
- V.-H. Karl, *Ang. Makromol. Chem.*, **79**, 11 (1979).
- L. Christmann and W. Knappe, *Colloid Polymer Sci.*, **252**, 705 (1974).
- L. Christmann, Dr. rer. nat.—Thesis, Technischen Hochschule Darmstadt, 1977.
- K. Helwege, W. Knappe, P. Paul, and V. Semjonow, *Rheol. Acta*, **6**, 165 (1967).
- R. S. Spencer and R. E. Dillon, *J. Colloid Sci.*, **3**, 163 (1948); *ibid.*, **4**, 241 (1949).
- K. K. Chee and A. Rudin, *Can. J. Chem. Eng.*, **48**, 362 (1970).
- R. Koningsveld, private communication.
- W. K. Moonan and N. W. Tschoegl, *Intl. J. Polym. Mater.*, **10**, 199 (1984).
- J. Y. Decroix and M. Hert, 5th Conf. Europ. Plast.—Caoutchouc, 1978, Proceedings, Paper No. E-9.

DISCUSSION: L. A. UTRACKI

J. Vlachopoulos: From the limited data that I have found in the literature and from some sample calculations that I made, I would not bother including the pressure dependence of viscosity for pressures up to 500 atm for common polymers, such as polystyrene and polyethylene. Maybe at levels of 1000 or 1500 atm there could be very large viscosity changes. From your experience and the published experimental data, do you see large changes at the lower pressure levels? A typical extrusion process may involve pressures of 500 or 600 atm. In injection molding the pressures may be much higher and there it could be very a significant increase.

L. A. Utracki: John, your assumptions are both correct and incorrect. The key is the magnitude of the temperature and the chain flexibility. At high $\tilde{T}$, or in practical terms at $T \gg T_g$, the free volume changes little with pressure. This is illustrated in Fig. A. Here, for an infinitely long, flexible chain ($s = 3c = \infty$) the packing parameter Y , is plotted as a function of $\tilde{P}$. At high $\tilde{T}$ the dependence is much weaker than at low $\tilde{T}$. Since viscosity increases exponentially with Y , the pressure does not have a large effect at high T . The attractiveness of the theory lies in the fact that you do not have to guess this. Knowing $\tilde{T}$ or T/T_g you can calculate how serious the pressure effect will be. For rigid molecules, with $u = 3c/s > 1$, the sensitivity to P is more pronounced. As an illustration you can take Christmann and Knappe data for HDPE and PMMA. Both polymers were tested in a range of pressures from 50 to 500 atm. In the first case (viz. series II) the viscosity increased by about a factor of 1.2, in the second by a factor of 3.7. The difference in pressure

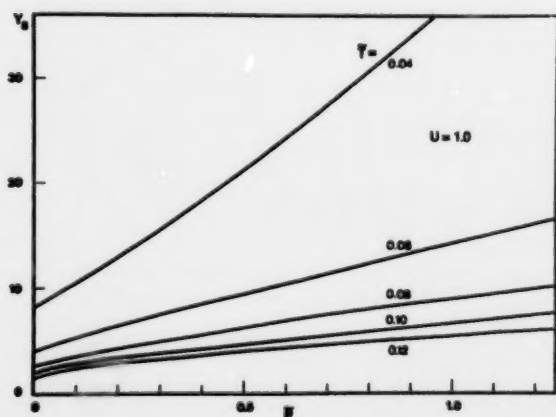


Fig. A. Theoretical correlation between the packing factor, Y , and reduced pressure, $\tilde{P}$, for polymers (flexibility parameter $U = 3c/s = 1$) at the indicated reduced temperatures, $\tilde{T}$.

sensitivity is clearly visible when comparing Figs. 25 and 27. Thus in some cases, even for modeling of extrusion, the assumption that viscosity does not change with P may lead to a serious error.

H. H. Winter: Certainly in injection molding the pressures are very high and we should consider the influence of pressure dependence. For the moment let us assume that the density depends on the pressure and the viscosity depends on the density. If you mold at very high pressures, the process of filling will be over within a fraction of a second. We know that density changes are not instantaneous, but are delayed. The density will not have the equilibrium value which you are discussing. In injection molding we have atmospheric pressure initially and again after half a second. How can we relate the transient process to the long-term equilibrium data? Maybe the equilibrium data would overestimate the effect of pressure dependence.

L. A. Utracki: The aim of this paper has been to examine whether for polymer melts there is a correlation between the zero-shear viscosity and the thermodynamic free volume fraction (as computed from the Simha's theory). This is but a first step. As you saw, such a correlation exists and the pressure and temperature effects on the zero-shear viscosity can be described through this parameter. To apply this information to injection molding requires a series of additional steps. Of these the pressure and temperature dependence of high-shear viscosity and the transient effects are the most important. These will be tackled in the future.

H. H. Winter: What about the transient zero shear viscosity?

L. A. Utracki: This seems to be a confusion of terms. Instead, let us consider the relaxation time, which is proportional to the zero shear viscosity. For polymer melts τ_R is of the order ranging from a millisecond to a few seconds. Pressure will slow down the relaxations.

H. H. Winter: Which could mean long relaxation times even for density changes, so that the density might not change significantly during half a second.

L. A. Utracki: The compression wave will not depend on the shear relaxation times, calculated for translation of macromolecules. One has to consider the sonic wave propagation, which depends on segmental, not macromolecular, mobility. Experimentally, sound velocity (which for polymers under ambient conditions is about 2 km/s) was found to be proportional to density, i.e. the rate that the density increases should increase with P .

Exit Pressure Effects in Capillary Die Data

PIERRE J. CARREAU

*Department of Chemical Engineering
Ecole Polytechnique de Montréal
Montréal, Québec H3C 3A7*

LIONEL CHOPLIN

*Department of Chemical Engineering
Laval University
Québec G1K 7P4*

and

JEAN-ROBERT CLERMONT

*Institut de Mécanique de Grenoble
38402 Saint-Martin d'Hères Cedex
France*

The exit flow from a capillary is analyzed with the help of macroscopic mechanical energy and momentum balances. The analysis shows that primary normal stress differences cannot be determined from the exit pressures under the assumption that the flow is viscometric down to the exit. This assumption and the second one (made by Han [9]) that both slit and capillary exit pressures are the same would lead to unacceptable results. Published exit pressure data for polyethylene melts are shown to be unreliable because of large hole-pressure errors in the pressure measurements. Pressure profiles obtained with a thin tube technique for the flow of a poly(isobutylene) solution indicate that the flow does not remain fully developed near the exit. Moreover, it is shown that for this polymer solution the excess viscous dissipation at the exit contributes to approximately 90 percent of the exit pressure.

INTRODUCTION

It is well known that standard cone-and-plate rheometers cannot be used to measure normal stresses of polymer melts at high shear rate (in the range of shear rates of industrial importance). In the last two decades, a lot of effort has been devoted to other methods, mainly based on the analysis of the flow in a capillary: excess pressure losses, extrudate swell, reactive thrust, and more recently exit pressure. These measurements yield useful information on the elastic properties of polymeric materials, but none has been proven to be a valid measure of the normal stresses: drastic assumptions have to be made that cannot be verified for a large class of materials. The exit pressure measurement appears to be the most promising method, since it is believed that the velocity profile in a capillary remains fully-developed down to the exit so that only normal stresses contribute to the exit pressure.

Using a macroscopic mechanical energy balance, Choplin and Carreau (1) have shown that for the

flow of polymer solutions in a slit the exit pressure represents mostly excess viscous dissipation. The primary normal stress difference, evaluated at the wall of the slit, is then given by the following expression for the inertial flow of power-law fluids:

$$N_{1w} = (1 + \beta) \left[\frac{2 + \beta + 1/n}{2 + 1/n} \right] [P_s^* - (\rho \hat{E}_v)_{ex}] \quad (1)$$

P_s^* is the extrapolated value of the pressure profile at the exit, and $(\rho \hat{E}_v)_{ex}$ is the excess viscous dissipation per unit volume due to the flow rearrangement at the exit; n and β are power-law parameters in the expression of the viscosity:

$$\eta = m |\dot{\gamma}|^{n-1} \quad (2)$$

and of the primary normal stress difference:

$$N_1 = \sigma |\tau_{12}|^\beta \quad (3)$$

m and σ are material parameters dependent on the temperature and eventually on the pressure; $\dot{\gamma}$ and

τ_{12} are, respectively, the shear rate and the shear stress. Equation 1 is analogous to that derived by Boger and Denn (2) from a momentum balance:

$$N_{1w} = (1 + \beta) \left[P_w^* + \frac{L}{H} \tau_w \cdot \left(1 - \int_0^1 f(\xi; \tau_w, Re) d\xi \right) \right] \quad (4)$$

where L is the length of the slit, $2H$ its thickness; f is a function of the dimensionless distance from the exit ξ , of the shear stress evaluated at the wall of the capillary τ_w , and of the Reynolds number Re ; the integral takes into account the velocity rearrangement near the exit.

It is clear from either Eq 1 or 4 that the primary normal stress difference cannot be determined from the exit pressure unless the excess viscous dissipation (or velocity rearrangement) is negligible or can be estimated. Since both results are believed to be correct and β is in the range of 1 to 2 for polymers, the viscous dissipation or the velocity rearrangement effect at the exit cannot be ignored.

The purpose of this paper is to extend the previous analysis (1) to the flow in a capillary and to show from published data for polymer melts and solutions if it is possible to use the exit pressure as a measure of the normal stresses. For the capillary geometry, the problem is somewhat more complex since the secondary normal stress difference intervenes. However, we will assume that the second difference is small and proportional to the first difference.

THEORY

We consider the flow of polymer emerging from a capillary, as illustrated in Fig. 1. The results given below are based on the following assumptions: the flow is laminar and under steady state and isothermal conditions; the velocity profile is fully developed in the capillary at some distance from the exit; inertial or kinetic energy terms do not contribute significantly to the momentum or energy balance; and external forces on the emerging extrudate are negligible. The last two assumptions are reasonable for the flow of polymer melts or concentrated solutions for which the Reynolds number is normally very small.

Macroscopic Mechanical Energy Balance

The previous analysis of Choplin and Carreau (1) for the flow in a slit can be readily extended to the case of a capillary. The result of example 7.3-1 of Bird, Stewart, and Lightfoot (3) can be used to obtain a mechanical energy balance between section "I" and section "II" of the exit flow as illustrated by Fig. 1. For the steady-state flow of incompressible liquid with negligible gravitational effects, the mechanical energy balance is:

$$\Delta(\frac{1}{2} \rho \langle V_z^3 \rangle S) + \Delta(\langle p V_z \rangle S) + \Delta(\langle \tau_{zz} V_z \rangle S) + E_v = 0 \quad (5)$$

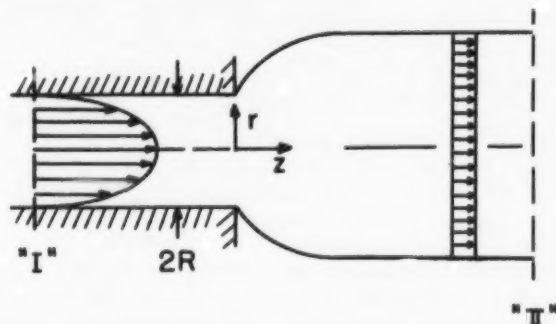


Fig. 1. Sketch of the exit flow from a capillary.

where Δ means value at section "II" minus value at section "I" and $\langle \rangle$ means average value over the flow section. This result includes a nonzero normal stress component τ_{zz} which is considered equal to zero for Newtonian fluids in Ref. 3. The first term of Eq 5 represents the contribution of the kinetic energy. This term is negligible for the flow of viscous polymers at low Reynolds number. E_v is the rate of energy dissipated by viscous forces over the entire volume of liquid between section "I" and section "II". The pressure and the normal stress in the extrudate, at a distance far enough from the exit, do not contribute to the mechanical energy balance since the velocity of the extrudate is very small and the rate of shear is equal to zero. Hence Eq 5 reduces to:

$$\int_{S_I} (p + \tau_{zz}) V_z dS - E_v = 0 \quad (6)$$

On the other hand, the r -component of the equation of motion for the fully-developed flow at section "I" is:

$$0 = -\frac{\partial p}{\partial r} - \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rr}) + \frac{\tau_{\theta\theta}}{r} \quad (7)$$

Integrating from r to R , we obtain:

$$P_w - (p + \tau_{rr}) = \int_r^R \frac{N_2(r)}{r} dr \quad (8)$$

where $P_w = (p + \tau_{rr})_{r=R}$ is the total pressure exerted on the wall of the capillary and $N_2 = -(\tau_{rr} - \tau_{\theta\theta})$ is the secondary normal stress difference. Eliminating the pressure p in Eq 6 with the use of Eq 8 and rearranging, we get:

$$P_w = \frac{2}{\langle V_z \rangle} \int_0^1 \left\{ N_1(\xi) - \int_1^\xi \frac{N_2(\xi)}{\xi} d\xi \right\} \cdot V_z(\xi) \xi d\xi + \frac{E_v}{\langle V_z \rangle} \quad (9)$$

where $N_1 = -(\tau_{zz} - \tau_{rr})$ is the primary normal stress difference and $\xi = r/R$.

In the fully-developed flow region, the wall pressure varies linearly with the distance from the exit and the exit pressure is defined as the extrapolated value of the linear profile down to the exit. Hence, from Eq 9, the exit pressure is given by:

$$P_c^* = \frac{2}{\langle V_z \rangle} \int_0^1 \left\{ N_1(\xi) - \int_1^\xi \frac{N_2(\xi)}{\xi} d\xi \right\} \cdot V_z(\xi) \xi d\xi + \frac{(E_v)_{ex}}{\langle V_z \rangle} \quad (10)$$

This result shows that the exit pressure is made up of two contributions: the stored (elastic) energy in the polymer chains expressed through the integral over the flow section of the normal stress differences evaluated in the fully-developed flow region, and the energy dissipated by viscous forces due to the flow rearrangement at the exit, i.e. the excess viscous dissipation $(E_v)_{ex}$. In the case of the slit flow, the secondary normal stress difference N_2 does not contribute to the stored energy. Equation 10 can be written in a dimensionless form in terms of an exit correction coefficient:

$$n_{ex} = \frac{P_c^*}{2\tau_w} = n_v + (n_v)_{ex} \quad (11)$$

where n_v and $(n_v)_{ex}$ are, respectively, the normal stress term and the excess viscous dissipation term at the exit.

A specific expression of the normal stress term can be obtained by assuming that power-law expressions (Eqs 2 and 3) describe adequately the viscosity and the primary normal stress difference. This is reasonable at large enough shear rate or shear stress. We further assume that the ratio of the secondary normal stress difference to the first difference is constant and equal to $-\epsilon$. From the few available data in the literature (Christiansen and Leppard (4), Leppard and Christiansen (5), and Keentok, *et al.* [6]), ϵ is small and in the range of 0.10 to 0.20. The velocity profile in the capillary is then:

$$V_z(\xi) = \langle V_z \rangle \left(\frac{3n+1}{n+1} \right) \left[1 - \xi^{\frac{n+1}{n}} \right] \quad (12)$$

and the normal stress term is:

$$n_v = \frac{\sigma |\tau_w|^{\beta-1}}{2} \left[\frac{6 + 2/n - \epsilon(\beta + 5 + 1/n)}{(\beta + 2)(\beta + 3 + 1/n)} \right] \quad (13)$$

Combining Eqs 3, 11, and 13, the primary normal stress difference evaluated at the wall of the capillary in the fully-developed flow region is given by the following expression:

$$N_{1w} = \left[\frac{(\beta + 2)(\beta + 3 + 1/n)}{6 + 2/n - \epsilon(\beta + 5 + 1/n)} \right] \quad (14)$$

$$\cdot [P_c^* - 2(n_v)_{ex}\tau_w]$$

This result can be used to determine the normal stresses from the exit pressure provided the excess viscous dissipation is negligible, and the parameters n , β , and ϵ are known.

Macroscopic Momentum Balance

Using a macroscopic momentum balance, Boger and Denn (2) have obtained analogous results. A

momentum balance over the control volume described by Fig. 1 for the inertial flow of polymers yields:

$$\int_0^{\tau_w} \{N_1(\tau_{12}) + \frac{1}{2}N_2(\tau_{12})\} \tau_{12} d\tau_{12} = \frac{\tau_w^2}{2} P_c^* + \frac{L}{R} \tau_w^3 \left(1 - \int_0^1 f(\xi; \tau_w, Re) d\xi \right) \quad (15)$$

where the function f describes the effect of the velocity rearrangement near the exit on the shear force acting on the wall of the capillary. This result can be put in two different usable forms: taking the derivative of each term of Eq 15 with respect to the shear stress τ_w , we obtain:

$$N_{1w} + \frac{1}{2}N_{2w} = P_c^* + \frac{\tau_w}{2} \frac{\partial P_c^*}{\partial \tau_w} + \frac{1}{\tau_w} \frac{\partial}{\partial \tau_w} \left[\tau_w^3 \frac{L}{R} \left(1 - \int_0^1 f(\xi; \tau_w, Re) d\xi \right) \right] \quad (16)$$

and evaluating the integrals for power-law liquids and assuming that $N_2 = -\epsilon N_1$, Eq 15 becomes:

$$N_{1w} = \frac{\beta + 2}{1 - \epsilon/2} \cdot \left[\frac{P_c^*}{2} + \frac{L}{R} \tau_w \left(1 - \int_0^1 f(\xi; \tau_w, Re) d\xi \right) \right] \quad (17)$$

(the factor 2 dividing P_c^* is missing in Eq 25 of Boger and Denn [2]). Comparing Eqs 14 and 17, which are based on the same assumptions, it is clear that these two results are compatible only if the excess viscous dissipation or the velocity rearrangement at the exit is important. In the absence of excess viscous dissipation, both results imply that $\epsilon = -\beta$. This is unacceptable since it is known that β is in the range of 1 to 2, whereas from reliable secondary normal stress data (4 to 6) ϵ is positive and in the range of 0.1 to 0.2.

Hypotheses of Han

In all their work on the subject, Han and coworkers (7 to 9) have implicitly assumed that the flow was fully developed down to the exit, i.e., $f(\xi; \tau_w, Re) = 1$. Under this condition, Eq 16 reduces to:

$$N_{1w} + \frac{1}{2}N_{2w} = P_c^* + \frac{\tau_w}{2} \frac{\partial P_c^*}{\partial \tau_w} \quad (18)$$

The corresponding result for the flow in a slit is:

$$N_{1w} = P_c^* + \tau_w \frac{\partial P_c^*}{\partial \tau_w} \quad (19)$$

Han (8, 9) observed that the exit pressures for the capillary and the slit flows were sensibly equal under the same conditions, i.e. $P_c^* = P_s^*$. It follows from Eqs 18 and 19 that:

$$N_{1w} = P_c^* \left[1 + \frac{\partial \ln P_c^*}{\partial \ln \tau_w} \right] \quad (20)$$

and

$$N_{2w} = -P_c^* \frac{\partial \ln P_c^*}{\partial \ln \tau_w} \quad (21)$$

Using these results, Han (8, 9) reported very large values of the parameter ϵ (between 0.4 and 0.6) for various polymer melts.

We further note that for power-law fluids ($N_{1w} = \sigma |\tau_w|^\beta$, and $-N_2/N_1 = \epsilon$), Eqs 20 and 21 give:

$$N_{1w} = \frac{P_c^*}{1 - \epsilon} \quad (22)$$

and

$$\epsilon = \frac{\beta}{1 + \beta} \quad (23)$$

This last relation is too restrictive, and values of ϵ are predicted to be too large since the parameter β is in the range of 1 to 2 for most polymers.

Like Boger and Denn (2), we seriously question the assumption of equal exit pressures for the slit and the capillary flows. If instead we assume that the secondary normal stress difference is proportional to the first difference, i.e. $N_2 = -\epsilon N_1$, Eq 17 reduces in the absence of velocity rearrangement to:

$$N_{1w} = \frac{\beta + 2}{2 - \epsilon} P_c^* \quad (24)$$

This result is different from Eq 20 in the sense that there is no restriction in Eq 24 on the parameter ϵ . Since the value of this parameter is believed to be small, Eq 24 should be more appropriate for the determination of the primary normal stress difference from the exit pressure provided the exit correction due to the flow rearrangement is not important.

ANALYSIS OF EXPERIMENTAL DATA

HDPE flow

First, we examine the data of high density polyethylene (HDPE) at two temperatures, 180 and 220°C. These data are taken from (9), problem 5.2, and Figs. 5.27 and 5.28 (we note that in a previous publication, the data for polyethylene and for polypropylene have been inverted (see Figs. 7 and 8 of Ref. 7). Han, *et al.* (7) claimed that no hole pressure errors were detected when measuring the pressure through a small hole for the flow of polymer melts. The exit pressure was obtained by extrapolating the pressure profile measured in the fully-developed flow region.

The exit pressure data are reported in Fig. 2 in term of n_{ex} . As shown by Han (9), both sets of data correlate well with the wall shear stress, with approximately no dependence on the temperature. We also present the data of Okubo and Hori (10) for HDPE at 170°C, obtained approximately from their reported values of $\bar{N}_w$, which is equal to P_c^* . In their case, the pressure was also measured through small taps made in the capillary wall. These

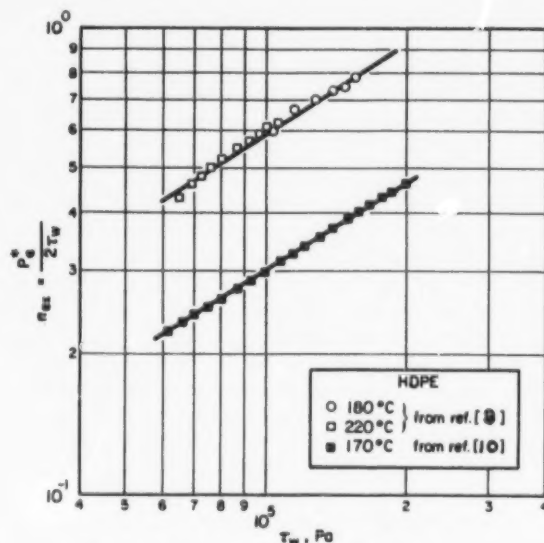


Fig. 2. Exit pressure data for HDPE melts.

data exhibit the same slope, but the values of n_{ex} are about one half of those of Han. The differences could possibly be attributed to differences in the HDPE molecular structure or molecular weight. We note that for both sets of data, n_{ex} is very small with values hardly higher than reported for Newtonian fluids (from a numerical solution, Nickell, *et al.* (11) have obtained a value of 0.265 for the flow of Newtonian fluids).

Using the data of Fig. 2, we have tested the hypotheses of Han. The slope of $\log n_{ex}$ versus $\log \tau_w$ is equal to 0.64; from the definition of n_{ex} and from Eqs 20 and 21, we obtain for Han's exit pressure data:

$$N_{1w} = 1.97 \times 10^{-3} |\tau_w|^{1.64} \quad (25)$$

$$\epsilon = -N_{2w}/N_{1w} = 0.62$$

Our calculations of the primary normal stress difference are shown in Fig. 3 (dash line) and compared to Han's cone-and-plate data (8). Unfortunately both sets of data do not overlap; nevertheless the predictions of Eq 20 appear to be on the low side. Using the same technique, Han reported somewhat higher values of N_1 . The value of ϵ obtained from Eq 21 is much too high, as one would expect from a comparison of reliable data in the literature. Han (9) has reported for the same set of data values of ϵ , increasing from 0.26 to 0.38 with increasing shear stress. However, in a previous publication (8), the same ratio is shown to decrease from 0.45 to 0.41. These low values are unexplained.

Removing Han's assumption of equal exit pressure for the slit and capillary flows, but retaining the assumption of fully-developed flow profile down to the exit, we also report in Fig. 3 the predicted normal stress differences as calculated from Eq 24. The parameter β is equal to 1.64, as before, and ϵ is taken as 0.1. These predictions are represented by the solid line. As expected, the

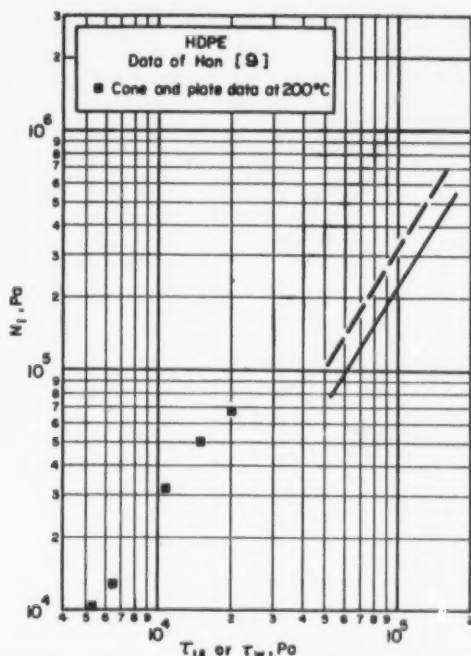


Fig. 3. Primary normal stress differences for a HDPE melt: ---- predictions from Eq 20, — predictions from Eq 24 with $\epsilon = 0.1$.

predictions are now lower and less acceptable when compared to the cone-and-plate data.

The assumption of fully-developed flow and that of no excess viscous dissipation at the exit of the capillary are equivalent. As shown in the previous section, the results of the macroscopic mechanical energy and momentum balances imply that $\epsilon = -\beta$. This is clearly unreasonable; moreover the predicted values of N_1 would even be lower than those shown in Fig. 3.

From this analysis the capillary exit pressure data of Han do not appear to be reliable, mainly due to complications in measuring pressure through small holes. Although questionable, the analysis of Higashitani and Pritchard (12) allows us to make an estimate of the hole-pressure errors. For a circular hole:

$$P_H = -\frac{1}{3} \int_0^{r_w} \frac{N_1(\tau_{12}) - N_2(\tau_{12})}{\tau_{12}} d\tau_{12} \quad (26)$$

which reduces for power-law fluids to:

$$P_H = -\frac{1 + \epsilon}{3\beta} N_{1w} \quad (27)$$

Hence the negative corrections can be as large as the exit pressures, as one can see from Fig. 3 by extrapolating the cone-and-plate data.

Okubo and Hori (10, 13) measured secondary normal stress differences of HDPE for the flow in an annular die (the apparatus is well-described in [13]). The secondary normal stress differences were determined from pressure readings through small holes with the assumption of negligible hole-pressure errors. They measured exit pressures from a

capillary die (10) and used Eq 18 to calculate $(N_1 + N_2/2)$. The values of N_1 were then obtained by subtracting $N_2/2$. They found that N_2 was always positive and that the ratio of N_2/N_1 ranged from 0.15 to 0.45, depending on the resin used, and varied slightly with the shear rate. Their exit pressure data for resin 080 at 170°C are reported in Fig. 2 in term of n_{ex} . Using Eq 18, we have calculated $N_1 + N_2/2$ and N_1 .

Our calculations are represented by the dash lines in Fig. 4 and compared to Okubo and Hori's results for 190°C (no exit data are reported for that temperature). Their calculations, shown by the solid lines, are much higher than ours, by approximately a factor of two. Such a difference cannot be explained by an effect of temperature, expected to be small when the results are plotted as a function of the shear stress. Strangely enough the same factor of two appears in Fig. 2 when we compare their exit data with those of Han. We suspect that their reported exit data are erroneous. It is doubtful that the values of N_2 could be positive and be as large with respect to N_1 , as shown by our calculations. As for the work of Han (7 to 9), the data of Okubo and Hori (10, 13) were obtained from pressure measurements through small holes and are unreliable due to hole-pressure errors.

Solution Flow

Clermont (14) has reported a few pressure profiles for the flow of a poly(isobutylene) (PIB) solution in a capillary, obtained with a thin tube technique. It consists of strain-gages mounted on the outside surface of a thin tube of 0.1 mm thickness and 4.95 mm diameter. The pressure is then measured indirectly from the tube deformation. This technique avoids the complication of hole-pressure errors, but the pressures have to be large enough to be measurable.

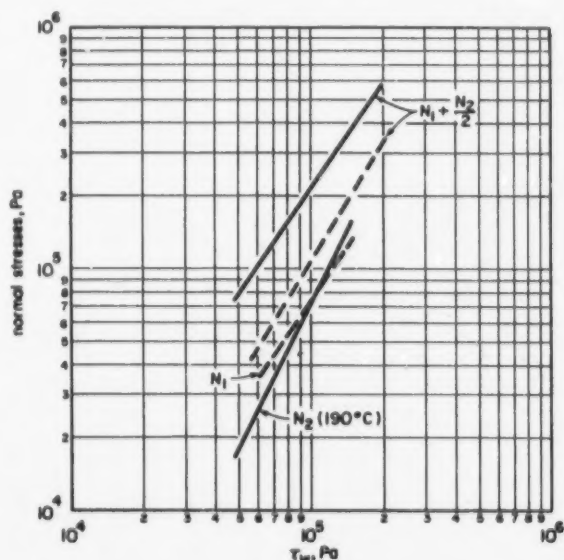


Fig. 4. Normal stress data for a HDPE melt, data of Okubo and Hori (10, 13).

Two pressure profiles are shown in Fig. 5 for the flow of a 50 percent (by weight) of PIB (Vistanex LMMS) in a mineral oil (Bayol 80). These data correspond to the largest flow rates. The pressure measurements at lower flow rates were not accurate enough for the determination of the exit pressure. As shown in Fig. 5, the pressure readings near the tube exit are considerably lower than expected from the linear profile. These data demonstrate that the assumption of viscometric flow down to the exit is not acceptable, and one would expect important excess viscous dissipation from the increase of the shear stress at the wall.

The two exit pressure data (extrapolated values shown in Fig. 5 and primary normal stress difference data are reported in Fig. 6. The cone-and-plate data, obtained on two different Weissenberg rheogoniometers and at two temperatures, show excellent agreement. The predicted primary normal stress differences from the exit pressures using Han's hypotheses (Eq 20) do not extrapolate the cone-and-plate data. First we note that under Han's hypotheses, the ratio of $-N_2/N_1$ is equal to 0.63, which is clearly unrealistic for such a polymer solution. Secondly, using the cone-and-plate data, we have calculated the n_{ψ} and $(n_r)_{ex}$ terms appearing in the macroscopic mechanical energy balance (Eq 11). The power-law index n , obtained from the viscosity data (14), is equal to 0.76. The results are shown in Table 1 for two different values of the parameters ϵ , 0 and 0.1. Clearly the excess viscous dissipation term is dominant; the normal stresses contribute only to approximately 10 percent of the exit pressure. The effect of a negative secondary normal stress difference (positive ϵ) is to decrease the contribution of the normal stresses to the exit pressure. Hence unless the secondary difference is positive and very large, most of the exit pressure represents energy dissipated due to a velocity rearrangement. These findings confirm our results (1) for the flow in a slit, which show that the excess viscous dissipation was the dominant factor although the sec-

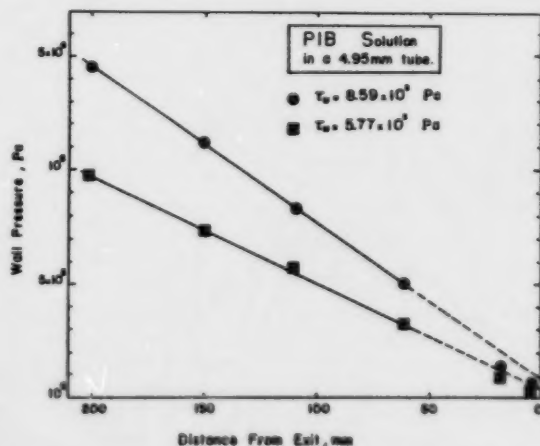


Fig. 5. Pressure profiles for the flow of a PIB solution in a capillary.

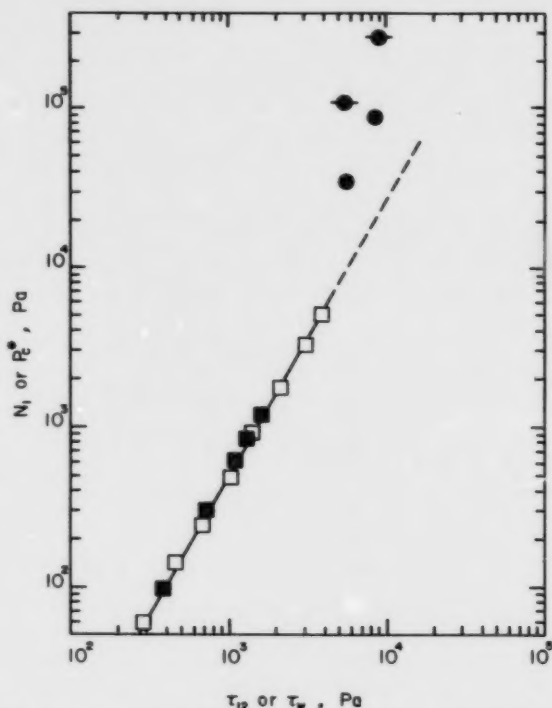


Fig. 6. Primary normal stress differences and exit pressure data for a PIB solution: $\square$ cone and plate normal stress data at 25°C, $\blacksquare$ cone and plate normal stress data at 20°C, $\bullet$ exit pressure data, $\blacklozenge$ predictions of primary normal stress differences from Eq 20.

Table 1. Exit Pressure Effects for the Flow of a PIB Solution in a 4.95 mm Tube.

τ_w (Pa)	$n_{ex} = \frac{p_e^0}{2\tau_w}$	n_s		$(n_r)_{ex}$	
		$\epsilon = 0$	$\epsilon = 0.1$	$\epsilon = 0$	$\epsilon = 0.1$
5.77×10^3	2.98	0.138	0.288	2.66	2.69
8.59×10^3	5.09	0.423	0.384	4.67	4.71

The rheological parameters are $n = 0.758$, $\alpha = 3.24 \times 10^{-2} \text{ Pa}^{-0.72}$, and $\beta = 1.72$.

ondary normal stress difference does not make any contribution to the exit pressure in that geometry.

Under the assumption of viscometric flow down to the exit, the primary normal stress differences obtained from the exit pressures may be considerably overestimated. Conversely, Han's assumption of equal exit pressures for the slit and capillary flows results in negative secondary normal stress differences that are too large. Both effects may, by coincidence, cancel out. And this is without considering possible errors in the measurements of the pressure.

CONCLUSIONS

The analysis of the exit flow from a capillary, based on both a macroscopic mechanical energy balance and a momentum balance, shows that the excess viscous energy dissipation or the velocity rearrangement near the exit cannot be neglected. Hence the exit pressures cannot be used to deter-

mine the primary normal stresses of polymer melts or solutions.

We seriously question the reliability of capillary exit pressures obtained from pressure measurements through small holes in the capillary wall, mainly due to complications of hole-pressure errors. Because of large hole effects, the published exit pressure data for polymer melts cannot be used to test the validity of the drastic assumptions necessary for the determination of normal stresses.

We have reported pressure profiles and exit pressures, obtained with a thin tube technique, for the flow of a polymer solution. These data show clearly that the flow is not viscometric near the exit. The excess viscous dissipation represents 90 percent of the exit pressure. This needs to be elucidated with more and accurate data. Further work is being done using the thin tube technique and a slit die with flush-mounted transducers; this will be reported elsewhere.

ACKNOWLEDGMENT

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NOMENCLATURE

E_c	= Rate of energy dissipated by viscous forces, W.
$\hat{E}_v$	= Energy dissipated per unit mass of liquid, m^2/s^2 .
f	= Function describing the effect of flow rearrangement at the exit.
H	= Half-thickness of slit, m .
m	= Power-law parameter in Eq 2, $Pa \cdot s^n$.
n	= Power-law index in Eq. 2.
n_{ex}	= Exit correction term defined by Eq 11.
$(n_v)_{ex}$	= Contribution of the excess viscous dissipation to the exit correction term.
n_4	= Contribution of the liquid's elasticity to the exit correction term.
N_1	= Primary or first normal stress difference, Pa.
N_2	= Secondary normal stress difference, Pa.
L	= Length of capillary or slit, m .
p	= Pressure, Pa.
p_H	= Hole-pressure error, Pa.
P_w	= Total pressure exerted on capillary wall, Pa.
P_c°	= Exit pressure for capillary flow, Pa.
P_s°	= Exit pressure for slit flow, Pa.
r	= Radial position, m .
R	= Radius of capillary, m .
Re	= Reynolds number.
S	= Flow section, m^2 .
V_z	= Liquid's velocity, m/s .

Greek Letters

β	= Parameter in Eq 3.
$\dot{\gamma}$	= Shear rate, s^{-1} .

ϵ	= Negative ratio of the secondary normal stress difference to the first difference.
ξ	= Dimensionless axial distance from exit.
η	= Non-Newtonian viscosity, $Pa \cdot s$.
ρ	= Liquid's density, kg/m^3 .
σ	= Parameter in Eq 3, $Pa^{1-\beta}$.
τ_{12}	= Shear stress, Pa.
τ_w	= Shear stress evaluated at the wall, Pa.
τ_{rr}	= Normal stress component in the r -direction, Pa.
$\tau_{\theta\theta}$	= Normal stress component in the θ -direction, Pa.
τ_{zz}	= Normal stress component in the z -direction, Pa.

Subscripts

ex	= Evaluated at the exit.
w	= Evaluated at the wall.

REFERENCES

1. L. Choplin and P. J. Carreau, *J. Non-Newt. Fluid Mech.*, **9**, 119 (1981).
2. D. V. Boger and M. M. Denn, *J. Non-Newt. Fluid Mech.*, **6**, 163 (1980).
3. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, N.Y. (1960).
4. E. B. Christiansen and W. R. Leppard, *Trans. Soc. Rheol.*, **18**, 65 (1974).
5. W. R. Leppard and E. B. Christiansen, *AIChE J.*, **21**, 999 (1975).
6. M. Keentok, A. G. Georgescu, A. A. Sherwood, and R. I. Tanner, *J. Non-Newt. Fluid Mech.*, **6**, 303 (1980).
7. C. D. Han, M. Charles, and W. Philippoff, *Trans. Soc. Rheol.*, **14**, 393 (1970).
8. C. D. Han, *Trans. Soc. Rheol.*, **18**, 163 (1974).
9. C. D. Han, "Rheology in Polymer Processing," Academic Press, New York (1976).
10. S. Okubo and Y. Hori, *J. Rheol.*, **23**, 625 (1979).
11. R. E. Nickell, R. I. Tanner, and B. Caswell, *J. Fluid Mech.*, **65**, 189 (1974).
12. K. O. Higashitani and W. G. Pritchard, *Trans. Soc. Rheol.*, **16**, 687 (1972).
13. S. Okubo and Y. Hori, *J. Rheol.*, **24**, 275 (1980).
14. J. R. Clermont, Doctoral Thesis, Institut National Polytechnique de Grenoble (1981).

DISCUSSION: P. J. CARREAU, "EXIT PRESSURE EFFECTS IN CAPILLARY DIE DATA"

J. Vlachopoulos: The exit corrections for the mechanical energy balance seem a little high. You gave a value around five. My impression was that it should have been smaller.

P. J. Carreau: This is not uncommonly high. I can show some of the data we have for a slit die. The excess viscous dissipation term at the exit for a typical viscoelastic fluid such as a 1.5 percent separan AP30 in a mixture of water and glycerol in a slit die goes almost as high as 10.

J. Vlachopoulos: How much would the Bagley correction be?

P. J. Carreau: The Bagley correction would be very high for this fluid, maybe close to 50.

L. Utracki: It seems evident that the exit pressure effect can not be used to measure the first normal stress difference, but you didn't mention anything about the other competing techniques, namely, the pressure-hole method. What method would you recommend for the measurement of the first and second normal stress differences at high shear rates?

P. J. Carreau: I was asked that same question at a recent symposium by industrial people who were very anxious to have a method to measure normal stresses at high shear rates. Perhaps extrudate swell is as good as anything else. It is a fairly easy measurement, but it may contain a lot of complexities that we don't fully understand. For the capillary flow I would prefer to use the Bagley correction, which is a measure of the excess viscous dissipation but which can be possibly related to the recoverable shear through cross correlation. However, it is unsafe to extrapolate from this. From our work we found that there could be surprises when working with unknown fluids. For constant viscosity elastic fluids, (so-called Boger fluids) we found quite different results from those obtained for typical viscoelastic fluids.

L. A. Utracki: The problem with these methods, either the Bagley method or the recoverable shear strain measured by extrudate swell, is that they are only correct for fully developed flow. For plug flow these approaches are no longer valid. In all cases involving multiphase flow, plug flow is evident to the extent that we get very large elastic modulus (G') or normal stress differences (N_1 and N_2) and negligible extrudate swell. Therefore the capillary or slit flow can not be used to measure the first normal stress difference if the velocity profile departs significantly from the Poiseuille shape.

P. J. Carreau: For any flow where kinetic or orientation effects could be significant over an extended time period, no fully-developed flow is expected anywhere in the capillary. I would agree that this can happen in many instances, even with a homogeneous polymer melt. The effect of orientation needs to be explored more deeply even for simple systems. There are coupled effects such as orientation and disentanglement of polymer chains, and it is difficult to know exactly what is going on.

J. Vlachopoulos: You have shown results for exit pressures and entrance pressures. What is the contribution of the first normal stress difference to the excess pressure drop at the entry if the normal stresses become larger? Does the excess pressure drop become larger or smaller?

P. J. Carreau: From the mechanical energy balance

the normal stress term will give a negative contribution to the entrance. The excess viscous dissipation, however, may be much larger because of viscoelastic effects due to elongational or transient effects at the entrance. For a Boger fluid, the entrance correction could be lower than for a Newtonian fluid. At the exit, the normal stress contribution to the exit pressure is positive. Han has claimed that the exit pressure consists of only the normal stress term. Our claim is that the exit pressure is comprised of both the normal stress and excess viscous dissipation terms, and that the excess viscous dissipation accounts for about 75 to 90 percent of the exit pressure. However, the exit correction is approximately 25 percent of the entrance correction and it is quite difficult to determine accurately.

L. A. Utracki: What is the elongational viscosity of the Boger fluid? Is it proportional to the shear viscosity?

P. J. Carreau: From approximate and preliminary measurements, the elongational viscosity seems to be very large with respect to the shear viscosity. The elongational viscosity may contribute significantly to the entrance effect but also the shear viscosity due to the very high and rapidly changing shear rate at the wall of the capillary near the entrance. This situation is analogous to the stress growth experiment at the onset of steady shear rate with the well-known overshoot phenomena. Similar overshoots are expected, resulting in large increases of the entrance correction. We did not measure large entrance corrections for the Boger fluids that did not exhibit the overshoot phenomenon in the stress growth experiment. Some fluids, however, may show large entrance effects because of their very large elongational viscosity.

H. Winter: You use the term recoverable strain. Does that hold outside the linear viscoelastic region? It might hold.

P. J. Carreau: No. I use the term that has been commonly used in the literature to correlate entrance corrections.

H. Winter: This comes from the theory of linear viscoelasticity for a Lodge rubberlike liquid, but there seems to be some indication that it might hold outside this region.

P. J. Carreau: I didn't look into that. For me the recoverable strain is equivalent to a Weissenberg number. In his paper, J. Vlachopoulos referred to this number as a Deborah number and explained the differences between the two. I agree with him except that I would interchange the definitions.

A Numerical Study of the Effect of Normal Stresses and Elongational Viscosity on Entry Vortex Growth and Extrudate Swell

E. MITSOULIS,* J. VLACHOPOULOS,

*Department of Chemical Engineering
McMaster University
Hamilton, Ontario, Canada L8S 4L7*

and

F. A. MIRZA

*Department of Civil Engineering and Engineering Mechanics
McMaster University
Hamilton, Ontario, Canada L8S 4L7*

A general-purpose finite element program has been used to simulate the flow of a typical polystyrene melt in the entry and exit regions of a slit die. Instead of using a general viscoelastic constitutive equation, simplified models were used that include correlations based on experimental data available in the literature for the shear and elongational viscosities and the normal stresses. With such simple models convergence of the iterative scheme is extended to relatively high Deborah numbers ($De \approx 5$). The models predict vortex growth in the entry region and an increase of extrudate swell at the exit in qualitative agreement with experimental observations. It was found that the normal stresses are primarily responsible for these phenomena, while the elongational viscosity tends to increase the end (Bagley) correction and decrease the swelling.

INTRODUCTION

The numerical simulation of creeping flow fields in the entry and exit region of a die has been the object of many investigations in recent years. While finite difference methods can be used for some of these problems, the main emphasis has been on finite elements because of their ability to incorporate complicated geometrical boundaries. Most of the work involving viscoelastic fluids has concentrated mainly on two problems, namely flow in a 4:1 axisymmetric contraction and extrudate swell from long capillaries. Extensive reviews have been published recently (1, 2).

From the numerical viewpoint there are no special problems associated with the application of the finite element method to Newtonian and inelastic shear-thinning fluids under isothermal conditions. With nonisothermal problems, numerical instabilities are encountered when the Peclet number is sufficiently large. The instabilities can be eliminated by using upwinding techniques and/or by

refining the finite element grid (2, 3). With viscoelastic fluid models the numerical schemes fail to converge at a certain value of elasticity level, which is usually expressed as a dimensionless Weissenberg number (Ws) or Deborah number (De) or stress ratio (S_R) (4).

There is a large amount of experimental data in the literature on flow through dies. While the materials used are seldom adequately characterized from the rheological point of view, the following conclusions can be drawn: extrudate swell, excess pressure at the entry, exit pressure, and corner vortex size and intensity increase with the elasticity level (5).

Viscoelastic fluid models that have been used so far in the numerical simulations by various investigators include the second-order fluid, the Criminale-Ericksen-Filbey (CEF) fluid, the upper-convected Maxwell fluid, the White-Metzner fluid, the Oldroyd-B fluid, and the Phan Thien-Tanner fluid. The solution of any of the above models in the geometries encountered in entry and exit flow problems poses many difficulties. Due to stress singularities at the entrance corner to the die and

* Present address: Dept. of Chemical Engineering, Univ. of Ottawa.

at the die exit, a large number of elements must be concentrated in these areas. This affects computer memory and time for the calculations. The models also include many terms and require numerical differentiation of velocities and velocity gradients which may introduce additional errors. To avoid this the stresses must enter the computations as primary variables along with velocities and pressure. This amounts to six unknowns per node for the two-dimensional ($u, v, p, \tau_{xx}, \tau_{yy}, \tau_{xy}$) and seven unknowns per node for the axisymmetric problem ($u, w, p, \tau_{rr}, \tau_{\theta\theta}, \tau_{zz}, \tau_{rz}$).

Despite the sophistication of the above models and the powerful numerical techniques employed, the results have not been encouraging in several aspects. A major difficulty has been the numerical breakdown for relatively low elasticity levels ($De < 1$), while most viscoelastic phenomena become pronounced for $De > 1$. Except for the recent simulations by Crochet and Keunings (6, 7) the calculations have been performed for low elasticity levels and therefore the results obtained are uninteresting. The upper De or Ws number limit for convergence depends, among other things, on the finite element grid used. Keunings and Crochet (7) report the surprising observation that the convergence limit for a Phan Thien-Tanner fluid in the entry flow problem was increased by 3.5 times when the size of the element near the reentrant corner was decreased by 5. Several thousand variables and mainframe computer times in the tens of hours were required for some of these calculations.

With the exception of Keunings and Crochet's work (7) all simulations have failed to predict the well-known vortex growth and excess pressure drop increase with shear rate for entry flow. However, exit pressures and extrudate swell results, although over a limited Deborah number range, are in qualitative agreement with observations. It is not at all clear why most of the above models give reasonable predictions for the exit region of a die but totally erroneous results for the entry.

These findings and almost a decade's stalemate with the numerical convergence of the above invented viscoelastic models led us to the conclusion that there is no future in pursuing further calculations with models based on the principles of linear (or quasi-linear) viscoelasticity. Instead, a different approach is adopted here based on examining the effects of certain polymer melt properties. These include the shear viscosity, normal stresses, and elongational viscosity. Highly simplified constitutive models are used, which are valid in simple shear flow and employ correlations of material properties for a typical polystyrene melt. Our numerical simulations predict extrudate swell, exit pressures, excess entry pressure, and vortex size and strength increase in qualitative agreement with experimental observations on polymer melts.

CONSERVATION AND CONSTITUTIVE EQUATIONS

For two-dimensional incompressible flow, the continuity equation can be written as

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad (1)$$

The equation of conservation of momentum for creeping flow ($Re \ll 1$) simplifies to

$$0 = -\frac{\partial p}{\partial x} + \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} \quad (2)$$

$$0 = -\frac{\partial p}{\partial y} + \frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} \quad (3)$$

For two-dimensional flow, the constitutive equation for a generalized Newtonian fluid takes the form

$$\tau_{xx} = \eta(\dot{\gamma})\dot{\gamma}_{xx} \quad (4a)$$

$$\tau_{yy} = \eta(\dot{\gamma})\dot{\gamma}_{yy} \quad (4b)$$

$$\tau_{xy} = \eta(\dot{\gamma})\dot{\gamma}_{xy} \quad (4c)$$

where $\eta(\dot{\gamma})$ is the apparent viscosity, which is, in general, a function of the magnitude of the rate-of-strain $|\dot{\gamma}|$

$$|\dot{\gamma}| = \left[\frac{1}{2} \mathbf{I}_2 \right]^{1/2} = \left[\frac{1}{2} \{\dot{\gamma} : \dot{\gamma}\} \right]^{1/2} \quad (5)$$

$$= \left[\frac{1}{2} (\dot{\gamma}_{xx}^2 + \dot{\gamma}_{yy}^2 + 2\dot{\gamma}_{xy}^2) \right]^{1/2}$$

where

$$\dot{\gamma}_{xx} = 2 \frac{\partial v_x}{\partial x}, \quad \dot{\gamma}_{yy} = 2 \frac{\partial v_y}{\partial y}, \quad (6)$$

$$\dot{\gamma}_{xy} = \frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y}$$

For engineering calculations, the most widely-used function for the apparent viscosity is the power law

$$\eta = m |\dot{\gamma}|^{n-1} \quad (7)$$

which usually describes adequately shear viscosity versus shear rate data for $\dot{\gamma} > 5 \text{ s}^{-1}$.

Another useful representation is the Carreau model (8)

$$\eta = \eta_0 [1 + (\lambda |\dot{\gamma}|)^2]^{\frac{n-1}{2}} \quad (8)$$

which is valid both for low (Newtonian) and high (power-law) shear rates.

In viscometric flows the first and second normal stress differences N_1 and N_2 , respectively, are given by

$$N_1 = \tau_{xx} - \tau_{yy} = \Psi_1(\dot{\gamma})\dot{\gamma}_{xy}^2 \quad (9)$$

$$N_2 = \tau_{yy} - \tau_{xx} = \Psi_2(\dot{\gamma})\dot{\gamma}_{xy}^2 \quad (10)$$

where Ψ_1 and Ψ_2 are the first and second normal stress coefficients. Like the viscosity η these are, in general, functions of the magnitude of the rate-of-strain $|\dot{\gamma}|$.

Oda, *et al.* (9) have found that for a wide variety

of polystyrene (PS) melts, normal stress data obey a power-law relation of the form

$$N_1 = A\tau_{xy}^b \quad (11)$$

Recently, Han, *et al.* (10) have shown that such a correlation is also valid for several other polymer melts.

It is also well-known that N_2 is much smaller than N_1 . To simplify the calculations we may assume $\Psi_2 = 0$. Taking into account Eqs 9 and 11 we have

$$\Psi_1 = A\eta^b \dot{\gamma}^{b-2} \quad (12)$$

We can now define a stress ratio S_R as

$$S_R = \frac{(N_1)_w}{2\tau_w} = \frac{\Psi_1 \dot{\gamma}_w^2}{2\eta \dot{\gamma}_w} = \frac{\Psi_1}{2\eta} \dot{\gamma}_w = \lambda \dot{\gamma}_w = De \quad (13)$$

where $\dot{\gamma}_w$ is the shear rate for fully developed flow at the wall, λ is a relaxation time, and their product De is the Deborah number. Thus, there is an equivalence between S_R and De under the above definitions. In the present work we shall use the Deborah number defined by Eq 13 as a measure of elasticity level.

In order to study the effect of normal stresses on the flow of polymer melts, we have used the above relations and assumptions to modify the constitutive equation of the generalized Newtonian fluid, which now takes the form

$$\tau_{xx} = \eta(\dot{\gamma})\dot{\gamma}_{xx} + \Psi_1(\dot{\gamma})\dot{\gamma}_{xy}^2 \quad (14a)$$

$$\tau_{yy} = \eta(\dot{\gamma})\dot{\gamma}_{yy} \quad (14b)$$

$$\tau_{xy} = \eta(\dot{\gamma})\dot{\gamma}_{xy} \quad (14c)$$

It should be pointed out that the above simplified constitutive equations (Eqs 14), which we call Model A, are—strictly speaking—valid in simple shear flows. Nevertheless, we shall employ Model A in nonviscometric flows such as entry and exit flows from dies. Our reasoning is based on the observation that in both situations there is a dominant flow direction, namely the x-direction. Of course, Model A does not conform to the principles of tensorial invariance and objectivity of the stress tensor since its predictions depend upon the choice of the frame of reference. However, it is felt that such a model may be used to study the effect of first normal stress difference on the flow field.

A close inspection of Model A shows that for low shear rates (very slow flows), the viscosity η is constant and equal to η_0 , if the Carreau model is used. In simple elongational flow, the term $\Psi_1 \dot{\gamma}_{xy}^2$ vanishes and the model predicts an elongational viscosity $\eta_T = 3\eta_0$ (Trouton viscosity). Such elongational viscosities have been measured experimentally for several melts at low elongational rates (usually, $\dot{\epsilon} < 10 \text{ s}^{-1}$). For higher rates, experimental data are very difficult to obtain and are not reliable. The general trends of elongational viscosity are shown in Fig. 1. For more detailed information the reader is referred to a recent comprehensive review (11). It can be seen that elongational viscosities start from the Trouton viscosity $\eta_T = 3\eta_0$ and may remain constant (PS), increase (LDPE), or decrease

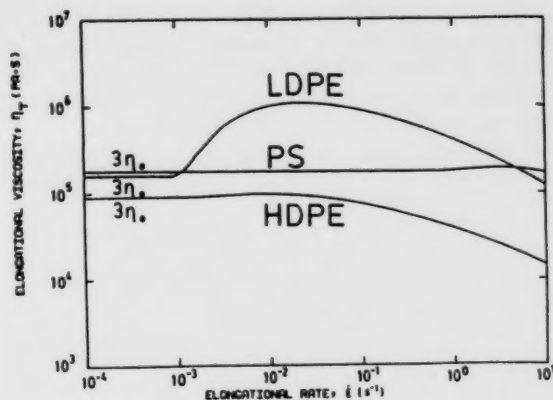


Fig. 1. Typical elongation viscosity versus elongational rate curves for polymer melts (based on H. M. Laun's and H. Münstedt's work, BASF, Ludwigshafen, W. Germany).

(HDPE) with increasing elongational rate (at least within the range of measurements). Since $\eta = \eta(\dot{\gamma})$ as given by both the power-law and the Carreau model decreases with $\dot{\gamma}$, it is evident that the elongational viscosity of Model A decreases as well with elongational rate. This is contrary to the experimental trends exhibited by PS melts.

In view of the above observations, we constructed a fluid model that obeys the following equations

$$\tau_{xx} = \eta_0 \dot{\gamma}_{xx} + \Psi_1(\dot{\gamma})\dot{\gamma}_{xy}^2 \quad (15a)$$

$$\tau_{yy} = \eta_0 \dot{\gamma}_{yy} \quad (15b)$$

$$\tau_{xy} = \eta(\dot{\gamma})\dot{\gamma}_{xy} \quad (15c)$$

The above fluid, which we call Model B, is essentially the same as Model A but has a constant viscosity η_0 for the τ_{xx} and τ_{yy} component. This modification amounts to having a constant elongational viscosity in simple elongational flow equal to Trouton viscosity for all elongational rates. Thus, Model B comes closer to representing experimental data on PS than Model A, as far as elongational flow is concerned, in the range of low elongational rates. The extrapolation of constant η_T assumed for higher elongational rates is arbitrary, and the results of the calculations could serve as an indication for the validity of such an assumption.

THE FINITE ELEMENT METHOD

The finite element method was developed using the primitive variable approach (velocities v_x , v_y , and pressure p) and was based on the principle of virtual work (12). The differential equation for conservation of momentum was written in an integral form as

$$\int_{\Omega} \sigma_{ij}(\delta v_i) d\Omega - \int_{\Omega} b_i(\delta v_i) d\Omega - \int_{\Gamma_i} T_i(\delta v_i) d\Gamma = 0 \quad (16)$$

where σ_{ij} is the total stress tensor, $\sigma_{ij} = -p\delta_{ij} + \tau_{ij}$, δ_{ij} is the Kronecker delta, and τ_{ij} is the extra stress

tensor; ϵ_{ij} is half the rate-of-strain tensor, $\delta\epsilon_{ij}$ is half the virtual rate-of-strain tensor, v_i is the velocity vector, δv_i is the virtual velocity vector, b_i are the body forces, Ω is the volume, and T_i are the surface tractions applied on part of the boundary Γ_t .

A second virtual work equation is required to incorporate incompressibility (continuity equation) and is of the following form:

$$\int_{\Omega} (\delta p) \frac{\partial v_i}{\partial x_i} d\Omega = 0 \quad (17)$$

where δp is the virtual pressure.

In the above we have made use of the definition of the half rate-of-strain tensor ϵ_{ij}

$$\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (18)$$

It should be noted that because of the symmetry of the ϵ_{ij} tensor, we get $\epsilon_{xy} = \epsilon_{yx}$. Thus, only three rate-of-strain components are needed for two-dimensional flows. This simplifies the finite element formulation by using a rate-of-strain vector $\{\epsilon\}$ with the following components

$$\{\epsilon\} = \begin{Bmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \dot{\gamma}_{xy} \end{Bmatrix} = \begin{Bmatrix} \frac{\partial v_x}{\partial x} \\ \frac{\partial v_y}{\partial y} \\ \frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \end{Bmatrix} \quad (19)$$

The stress tensor σ_{ij} is also reduced to a stress vector $\{\sigma\}$ with components σ_{xx} , σ_{yy} , σ_{xy} .

A constitutive relation between stresses and rates-of-strain is written in the form

$$\{\sigma\} = -p\{I\} + [D]\{\epsilon\} + \{\tau_0\} \quad (20)$$

where $\{I\}$ is the unit vector δ_{ij} , $[D]$ is a constitutive matrix, and $\{\tau_0\}$ a stress vector that accounts for all possible stresses present in the fluid that cannot be included in the product $[D]\{\epsilon\}$. For the generalized Newtonian fluid we have

$$[D] = \begin{bmatrix} 2\eta(\dot{\gamma}) & 0 & 0 \\ 0 & 2\eta(\dot{\gamma}) & 0 \\ 0 & 0 & \eta(\dot{\gamma}) \end{bmatrix}, \quad \{\tau_0\} = \{0\} \quad (21)$$

For Model A, $[D]$ remains the same, while $\{\tau_0\}$ contains the extra $\Psi_1 \dot{\gamma}_{xy}^2$ term, i.e.

$$\{\tau_0\} = \begin{Bmatrix} \Psi_1(\dot{\gamma}) \dot{\gamma}_{xy}^2 \\ 0 \\ 0 \end{Bmatrix} \quad (22)$$

For Model B we have

$$[D] = \begin{bmatrix} 2\eta_0 & 0 & 0 \\ 0 & 2\eta_0 & 0 \\ 0 & 0 & \eta(\dot{\gamma}) \end{bmatrix}, \quad \{\tau_0\} = \begin{Bmatrix} \Psi_1(\dot{\gamma}) \dot{\gamma}_{xy}^2 \\ 0 \\ 0 \end{Bmatrix} \quad (23)$$

The flow domain was discretized into triangular elements with six nodes for the velocities and three nodes for pressure. Quadratic interpolation functions for velocities and linear interpolation functions for pressure were used, i.e.

$$u = \langle N_x \rangle \{u^*\}, \quad v = \langle N_y \rangle \{v^*\}, \quad p = \langle N_p \rangle \{p^*\} \quad (24)$$

where $\langle \rangle$ denotes a row vector, $\{ \}$ denotes a column vector, * denotes nodal values, and N_i are the interpolation functions. The rate-of-strain vector $\{\epsilon\}$ is then approximated by

$$\{\epsilon\} = [B] \begin{Bmatrix} u^* \\ v^* \end{Bmatrix} = \begin{bmatrix} \frac{\partial \langle N_x \rangle}{\partial x} & 0 \\ 0 & \frac{\partial \langle N_y \rangle}{\partial y} \\ \frac{\partial \langle N_x \rangle}{\partial y} & \frac{\partial \langle N_y \rangle}{\partial x} \end{bmatrix} \begin{Bmatrix} u^* \\ v^* \end{Bmatrix} \quad (25)$$

where $[B]$ is the rate-of-strain matrix.

Substitution of the approximations (Eqs 24 and 25) back to the integral equations (Eqs 16 and 17) yields

$$[K_c] \begin{Bmatrix} u^* \\ v^* \end{Bmatrix} + [K_p] \{p^*\} = \{F_b\} + \{F_T\} - \{F_0\} \quad (26a)$$

$$[K_p]^T \begin{Bmatrix} u^* \\ v^* \end{Bmatrix} = \{0\} \quad (26b)$$

or

$$\begin{bmatrix} [K_c] & [K_p] \\ [K_p]^T & [0] \end{bmatrix} \begin{Bmatrix} \{u^*\} \\ \{p^*\} \end{Bmatrix} = \begin{Bmatrix} \{F\} \\ \{0\} \end{Bmatrix} \quad (26c)$$

(symmetric)

where

$$[K_c] = \int_{\Omega} [B]^T [D] [B] d\Omega \quad (27a)$$

$$[K_p] = \int_{\Omega} \{N_i\}_{,i} \langle N_p \rangle d\Omega \quad (27b)$$

$$[K_p]^T = \left[\int_{\Omega} \{N_i\}_{,i} \langle N_p \rangle d\Omega \right]^T \quad (27c)$$

$$= \int_{\Omega} \{N_p\} \langle N_i \rangle_{,i} d\Omega$$

$$\{F\} = \{F_b\} + \{F_T\} - \{F_0\} = \int_{\Omega} [N]^T \{b\} d\Omega \quad (27d)$$

$$+ \int_{\Gamma_t} [N]^T \{T\} d\Gamma - \int_{\Omega} [B]^T \{\tau_0\} d\Omega$$

Equation 26c takes the final form

$$[K]\{X^*\} = \{F\} \quad (28)$$

where $[K]$ is the global stiffness matrix containing the viscosity, $\{X^*\}$ is the vector of unknown veloci-

ties and pressures, and $\{F\}$ is the global load vector containing the extra stresses $\{\tau_0\}$ and boundary conditions (in the absence of body forces and surface tractions). The resulting algebraic system of equations (Eq 28) was solved by the Choleski decomposition method for banded symmetric matrices. Since both $[K]$ and $\{F\}$ are functions of $\{X^*\}$ through the strain-rate dependent viscosity η and first normal stress coefficient Ψ_1 , Eqs 28 are nonlinear and iterations are needed. The iterative scheme used was based on direct substitution of the previous velocity field to update both $[K]$ and $\{F\}$, starting from the Newtonian solution of constant viscosity η and $\Psi_1 = 0$. It was found that convergence was attained within 4 to 5 iterations for both Models A and B for relatively high Deborah numbers (in some cases up to 5.5) and that Model B had a much smoother convergence than Model A even for very high Deborah numbers. The overall good behavior of both models is apparently due to their simplicity. It is also believed that Model B exhibits a better convergence rate because of a stabilizing effect exerted by the constant viscosity on the solution while the contribution of $\Psi_1 \dot{\gamma}_{xy}^2$ increases in the τ_{xx} component.

From the solution of the velocity field the vorticity ω can be obtained from its definition

$$\omega = \frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y} \quad (29)$$

The Poisson equation for the stream function Ψ

$$\nabla^2 \Psi = -\omega \quad (30)$$

can then be solved to give the streamlines.

The solution of Eq 30 has been obtained by using a finite element formulation for the stream function. Using the virtual work method, Eq 30 is written in an integral form as

$$\int_{\Omega} \frac{\partial(\delta\Psi)}{\partial x_i} \frac{\partial\Psi}{\partial x_i} d\Omega + \int_{\Omega} (\delta\Psi)\omega d\Omega = 0 \quad (31)$$

where $\delta\Psi$ is the virtual stream function.

The flow field is discretized into three-node triangular elements by subdividing each velocity-pressure triangle into four stream function triangles. Linear interpolation functions for Ψ are employed, i.e.

$$\Psi = \langle N_{\Psi} \rangle \{ \Psi^* \} \quad (32)$$

Substitution of Eq 32 into the integral Eq 31 yields

$$[S] \{ \Psi^* \} + \{ \omega \} = \{ 0 \} \quad (33)$$

where $[S]$ is a stream function stiffness matrix and $\{ \omega \}$ is the load vector containing the vorticity. These are given by

$$[S] = \int_{\Omega} \left(\frac{\partial N_i}{\partial x} \frac{\partial N_j}{\partial x} + \frac{\partial N_i}{\partial y} \frac{\partial N_j}{\partial y} \right) d\Omega \quad (34a)$$

$$\{ \omega \} = \int_{\Omega} N_i \omega d\Omega \quad (34b)$$

The linear system of equations (Eq 33) is solved for

the nodal unknowns Ψ^* by the Choleski decomposition method. The stream function values are then normalized and contour plots are obtained for the streamlines.

RESULTS AND DISCUSSION

Die Entry Flow

The isothermal version of our MACVIP finite element program (13) was used for simulation of entry flow in slit dies at very low Reynolds numbers ($Re < 10^{-3}$). While several geometries have been examined, the results presented in this paper are for a 10:1 planar sudden contraction. For such a contraction ratio the reservoir pressure drop is negligible. It can thus be assumed that such results are also reasonably good approximations for entry flow from an infinite reservoir. The die shape and dimensions are shown in Fig. 2 (inset) along with the finite element grid. Such a grid consists of 200 elements, 459 nodes, and gives a total of 881 degrees of freedom. The Newtonian problem requires 200 CPU seconds in McMaster's CDC-6400/CYBER 170 computer.

Preliminary calculations were performed with Model A and a shear viscosity for a typical polystyrene melt given by a power-law model

$$\eta = m |\dot{\gamma}|^{n-1} \text{ (Pa} \cdot \text{s)} \quad (35a)$$

with

$$m = 9500 \text{ Pa} \cdot \text{s}, \quad n = 0.38 \quad (35b)$$

The normal stress data were obtained from Oda, et al. (9) and are given by another power-law model

$$N_1 = A \dot{\gamma}_{xy}^b \text{ (Pa)} \quad (36a)$$

with

$$A = 3.47 \times 10^{-3} \text{ Pa}^{1-b}, \quad b = 1.66 \quad (36b)$$

The above correlation was obtained from low shear rate measurements ($\dot{\gamma} < 10 \text{ s}^{-1}$) but due to lack of any other experimental data is used here for extrapolation for $\dot{\gamma} > 10 \text{ s}^{-1}$ as well. The first normal stress coefficient Ψ_1 is then given by

$$\begin{aligned} \Psi_1 &= \frac{N_1}{\dot{\gamma}_{xy}^2} = \frac{A |m| \dot{\gamma}^{n-1} \dot{\gamma}_{xy}^b}{\dot{\gamma}_{xy}^2} \\ &= A m^b |\dot{\gamma}|^{(n-1)b} \dot{\gamma}_{xy}^{b-2} \text{ (Pa} \cdot \text{s}^2) \end{aligned} \quad (37)$$

The Deborah number is given by

$$De = \frac{(N_1)_w}{2\tau_w} = \frac{A}{2} m^{b-1} \dot{\gamma}_w^{n(b-1)} = 0.732 \dot{\gamma}_w^{0.25} \quad (38)$$

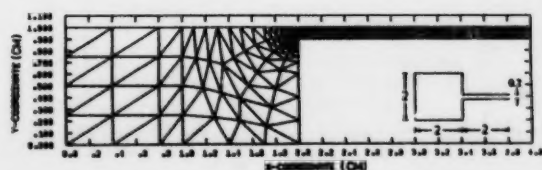


Fig. 2. Finite element grid for die entry flow and die dimensions (inset).

We note that De increases as $\dot{\gamma}_w$ increases.

For the finite element calculations we impose a fully developed power-law velocity profile at the upstream and downstream planes, zero velocities at the wall (no slip condition) and zero v_y component at the symmetry line. We also specify the pressure to be zero at one point (here at the exit wall). Runs were carried out for $De = 2.15, 2.7$, and 4.0 . The vortex size and intensity remained essentially unchanged and close to the inelastic values (4) even for the case of such high elasticity level as $De = 4$, which corresponds to $\dot{\gamma}_w = 908 \text{ s}^{-1}$. We conclude therefore that Model A with a power-law viscosity does not produce the strong vortices expected from experimental studies on polystyrene melts (14). The pressure drop was also found to decrease with elasticity, which again is not corroborated by general experimental trends for polymer melts (5, 15).

In our effort to represent more realistically the behavior of polymer melts we noticed that the flow in the reservoir corners remains very weak compared with the flow in the slit, even for high flow rates. Weak flows are basically Newtonian in shear, exhibiting a constant viscosity. Therefore the Carreau model (Eq 8) comes much closer to representing the Newtonian behavior at low shear rates and the shear-thinning behavior at high shear rates than the power-law model.

Figure 3 shows experimental viscosity data for a commercial polystyrene melt (Dow Styron 678 U at 180°C) as given by Huang and White (16). The data are fitted using the Carreau model with

$$\eta_0 = 9500 \text{ Pa}\cdot\text{s}, \lambda = 1.148 \text{ s}^{-1}, n = 0.50 \quad (39)$$

or

$$\eta = 9500 [1 + (1.148 |\dot{\gamma}|)^2]^{-0.25} (\text{Pa}\cdot\text{s}) \quad (40)$$

The Carreau curve is also drawn in Fig. 3, and a good agreement is obtained for both low and high shear rates.

Due to the nonlinearity of the Carreau model, analytical expressions for the velocity profiles in fully developed Poiseuille flow cannot be obtained. A fourth-order Runge-Kutta method was employed

to solve the momentum equation for flat plates. The shear rate, velocity, and stream function profiles were obtained as well as the average velocity and flow rate for the dimensions of the slit. For fully developed flow in the reservoir, the Runge-Kutta program was again employed and iterations were performed to obtain the velocity profile that would give the same flow rate as in the slit, thus satisfying mass conservation requirements. The so-obtained profiles were then used as boundary conditions in the finite element programs. The accuracy of the Carreau velocity profiles at the reservoir entry and the slit exit was checked using the criterion of a flat pressure profile between the wall and centerline, which was always met within less than 0.1 percent in the FEM solutions.

The first normal stress coefficient Ψ_1 is now given by

$$\begin{aligned} \Psi_1 &= \frac{N_1}{\dot{\gamma}_{xy}^2} = \frac{A(\eta \dot{\gamma}_{xy})^b}{\dot{\gamma}_{xy}^2} \\ &= \frac{A\{\eta_0[1 + (\lambda |\dot{\gamma}|)^2]^{\frac{n-1}{2}} \dot{\gamma}_{xy}\}^b}{\dot{\gamma}_{xy}^2} \\ &= A\eta_0^b [1 + (\lambda |\dot{\gamma}|)^2]^{\left(\frac{n-1}{2}\right)b} \dot{\gamma}_{xy}^{b-2} \end{aligned} \quad (41)$$

The Deborah number is given by

$$\begin{aligned} De &= \frac{(N_1)_w}{2\tau_w} = \frac{A}{2} \tau_w^{b-1} \\ &= \frac{A}{2} \eta_0^{b-1} [1 + (\lambda \dot{\gamma}_w)^2]^{\left(\frac{n-1}{2}\right)(b-1)} \dot{\gamma}_w^{b-1} \end{aligned} \quad (42)$$

and it is an increasing function of $\dot{\gamma}_w$, the wall shear rate.

Calculations were performed using both Model A and B for a series of Deborah numbers that correspond to both very low and very high shear rate flows. Rapid convergence of the numerical scheme was obtained within four to five iterations. It was noted, however, that for high Deborah numbers ($De \geq 4.5$), the numerical scheme for Model A converged within the first four iterations, but then diverged with increasing number of iterations. Therefore, the results reported here for $De \geq 4.5$ are from the fourth iteration (minimum value of the norm-of-the-error criterion for convergence). Model B always exhibited a rapid monotonic convergence for all De numbers examined.

The flow fields for different De numbers are shown in Fig. 4 for Model A and Fig. 5 for Model B. Both models predict an increase of vortex size with elasticity as expected from experimental observations for PS melts (14) and polymer solutions (17).

The entrance correction is defined by

$$n_{en} = \frac{\Delta P - (\Delta P_{res} + \Delta P_{sl})}{2\tau_w} \quad (43)$$

where ΔP_{res} is the pressure drop for fully developed flow in the reservoir alone (≈ 0), ΔP_{sl} is the pressure drop for fully developed flow in the slit and τ_w the

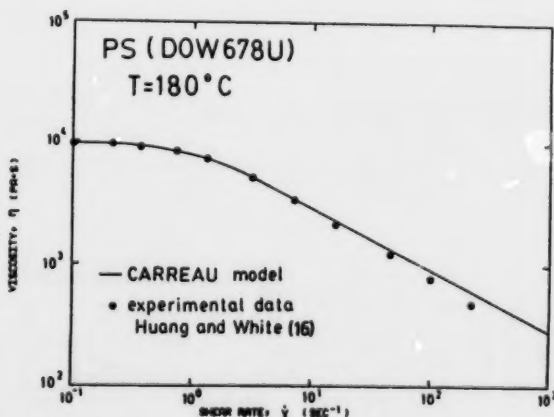


Fig. 3. Shear viscosity data for a PS melt and Carreau model representation.

PS: MODEL A

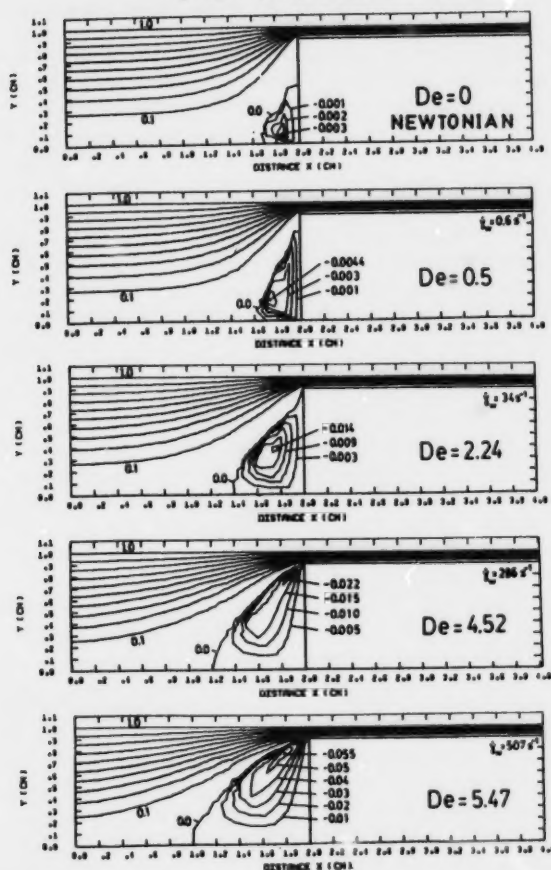


Fig. 4. Flow patterns for different De numbers in a 10:1 planar contraction (PS melt, Model A).

PS: MODEL B

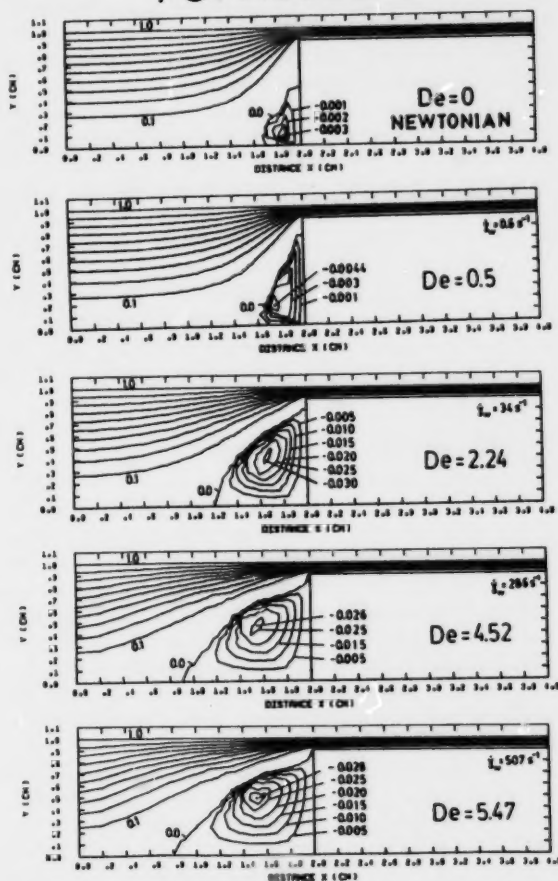


Fig. 5. Flow patterns for different De numbers in a 10:1 planar contraction (PS melt, Model B).

shear stress at the slit wall. Figure 6 shows the entrance correction as a function of De for both models. While Model A predicts a rapid decrease with De , Model B predicts an increase, which is also expected from experimental results. Nevertheless, this increase is considered rather moderate and certainly lower than the experimentally obtained values, which are in the range 1–10 for $\dot{\gamma}_w$ around 100–350 s^{-1} (5). It is quite possible, though, that the elongational viscosity of PS for high elongational rates is much higher than the Trouton viscosity of $3\eta_0$ adopted in Model B. Our results from the two models clearly demonstrate that the entrance correction depends on the elongational viscosity as introduced through the τ_{xx} and τ_{yy} stress components. A test run for a fluid that obeyed an exponential dependence in the form

$$\tau_{xx} = [\eta_0 \exp(\dot{\gamma}_{xx})] \dot{\gamma}_{xx} + \Psi_1 \dot{\gamma}_{xy}^2 \quad (44a)$$

$$\tau_{yy} = [\eta_0 \exp(\dot{\gamma}_{yy})] \dot{\gamma}_{yy} \quad (44b)$$

with the usual expression for the shear stress

$$\tau_{xy} = \eta(\dot{\gamma}) \dot{\gamma}_{xy} \quad (44c)$$

gave entrance correction in the range mentioned above and also large vortices of considerable

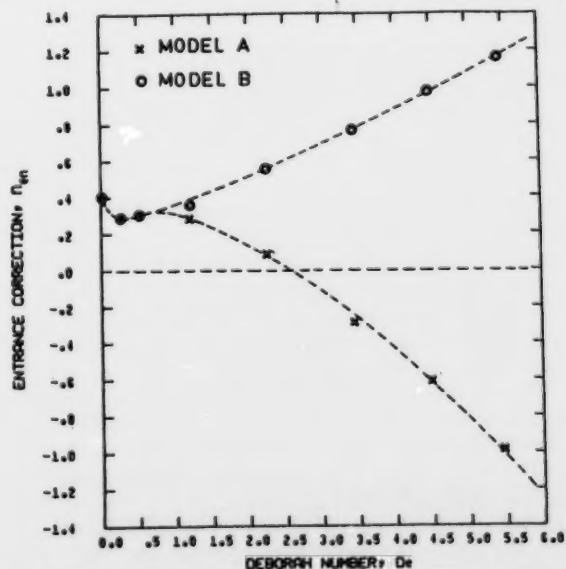


Fig. 6. Entrance correction versus Deborah number as predicted by Models A and B (PS melt).

strength. On the other hand, exclusion of the normal stress term $\Psi_1 \dot{\gamma}_{xy}^2$ eliminated the vortices, but

the entrance correction was even higher. These results seem to support the statement by White (5) that "a nonlinear increasing elongational viscosity in a fluid which does not exhibit shear flow normal stresses will not produce vortices".

The reduction of entrance correction as the wall normal stress increases is fully in agreement with the ideas of Choplin and Carreau (18). Such a reduction means that as the normal stress increases the fluid is "pulled through" faster. The pulling action leads to vortex size and intensity increase for the appropriate balance of normal and shear stresses. The power-law model for shear viscosity failed to predict vortex growth because the apparent viscosity becomes unrealistically large as $\dot{\gamma} \rightarrow 0$ in the reservoir corner, thus giving rise to very high shear forces in the reservoir.

Die Exit Flow and Extrudate Swell

It is well known that the flow of polymeric liquids from dies is accompanied by considerable swelling of the emerging jet. Consequently, the finite element mesh must be allowed to take the shape of the extrudate. The mesh must also contain many elements near the die exit to capture the drastic changes occurring there due to changing boundary conditions and to a stress singularity right at the die exit corner. Taking into account several studies (4), we developed a mesh consisting of 184 triangular elements with 423 nodes and 859 degrees of freedom, as shown in Fig. 7. The die and extrudate lengths are equal to eight times the die gap width. The free surface is determined iteratively as explained by Mitsoulis, *et al.* (4).

Preliminary calculations were performed with Model A and a power-law model viscosity as given by Eqs 35 for a typical PS melt. Equations 36, 37,

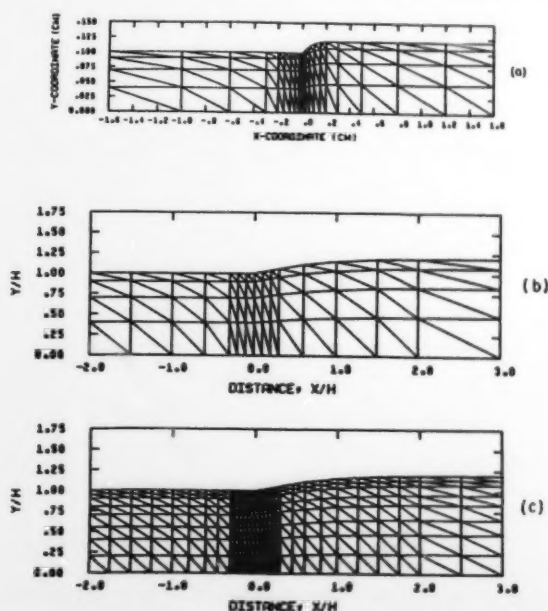


Fig. 7. (a) Finite element grid for die exit flow, (b) detailed grid near the die exit (velocity-pressure triangles), (c) detailed grid near the die exit (stream function triangles).

and 38 also remain the same. For the finite element calculations we impose a fully developed power-law velocity profile at the upstream plane, a flat velocity profile at the downstream extrudate plane that satisfies the same flow rate, zero velocities at the wall (no slip condition), and zero v_y component at the symmetry line. We also specify the pressure to be zero at one point (here at the downstream extrudate centerline).

The solution process started from the inelastic, shear thinning case (see Mitsoulis, *et al.* (4)). Successive small De number increments were used. Each incremental step consisted of four iterations on the free surface intertwined with two iterations on the algebraic system. It was found that four iterations on the free surface were sufficient to meet our criterion of less than 1 percent change of the final swell ratio. Using Model A, with a power-law shear viscosity, swelling ratios h/H up to 1.085 for $De = 1.5$ were obtained. Further Deborah number increases did not produce larger swelling ratios and the calculations with the power-law viscosity were abandoned. To avoid the unrealistically high apparent viscosity values at $\dot{\gamma} \rightarrow 0$ the power-law was replaced by the Carreau model (Eqs 39 and 40). Both Model A and B were used and the numerical simulations were carried out for a series of Deborah numbers. The solution process starts from the Newtonian, inelastic case (i.e. swell ratio $h/H = 1.196$, see Mitsoulis, *et al.* (4)). Table 1 shows a typical solution process as obtained with Model A for $De = 2.0$. The initial domain is read in from the solution for $De = 1.75$ ($h_0/H = 1.480552$) and the algebraic system is solved iteratively (direct substitution, Picard method). A new surface is constructed ($h_1/H = 1.542965$) and two iterations are performed in the new domain to yield a new surface ($h_2/H = 1.608226$). The procedure is repeated and then stopped after the fourth surface iteration with a relative error between the last two surfaces of 0.27 percent. Improvement can be further achieved with more iterations, but due to the large costs involved four surface iterations were considered sufficient.

It was noted that for Model A and for $De > 2.0$ convergence of the free surface became more difficult to attain and the swell ratio was increasing very rapidly (Table 2). On the other hand, Model B always had a smooth convergence for De values

Table 1. Iterative Scheme for Extrudate Surface Determination (Model A, $De = 2.0$).

Iteration	norm-of-the-error	h/H	new surface h/H	$(h_{n+1} - h_n)/H \times 100$
initial	—	1.480552		
1st	9.26	1.480552		
2nd	2.16	1.480552	1.542965	6.24%
1st	122.91	1.542965		
2nd	0.74	1.542965	1.608226	6.53%
1st	125.48	1.608226		
2nd	0.39	1.608226	1.659296	5.10%
1st	127.32	1.659296		
2nd	0.30	1.659296	1.662045	0.27%

* Run time about 1/2 hr. CPU on the CDC-6400/CYBER-170 computer (225 CPU seconds per iteration).

Table 2. Exit Correction and Extrudate Swell for Different De Numbers as Predicted by Model A and B for the Flow of a PS Melt Through a Slit Die.

De	$\dot{\gamma}_w (s^{-1})$	$\tau_w (MPa)$	Model A		Model B	
			n_{ex}	h/H	n_{ex}	h/H
0	(all $\dot{\gamma}$)	(all τ)	0.153	1.196	0.153	1.196
0.5	0.60	0.0052	0.287	1.263	0.302	1.282
1.0	3.17	0.0155	0.446	1.300	—	—
1.2	5.15	0.0200	0.516	1.325	0.617	1.393
1.5	10.13	0.0282	0.614	1.402	—	—
1.75	16.02	0.0355	0.695	1.481	0.905	1.451
2.0	24.00	0.0435	0.788	1.662	1.031	1.477
2.08*			0.788*	1.650*		
2.24	34.06	0.0518	0.866	1.858	1.153	1.500
2.56*			0.877*	1.880*		
2.68	58.66	0.0680	~(1.037)	—	1.371	1.539
3.53*			1.025*	2.432*		
3.0	83.21	0.0810	—	—	1.531	1.571
3.46	126.80	0.1000	—	—	1.747	1.607
4.52	285.18	0.1500	—	—	2.246	1.688
5.47	506.84	0.2000	—	—	2.684	1.769

* Based on $N_1 = 3.4 \times 10^{-3} \tau_w^{2.18}$ ($\tau_w \leq 0.04$ MPa or $\dot{\gamma} \leq 20$ s $^{-1}$) (Huang and White (16)).
 $N_1 = 1.40 \times 10^{-3} (\dot{\gamma}_w^{2.18})$ ($\tau_w > 0.04$ MPa or $\dot{\gamma} > 20$ s $^{-1}$)

as high as 5.47 ($\dot{\gamma}_w = 507$ s $^{-1}$). The criterion of less than 1 percent change for two successive surfaces was always met within four surface iterations. Nevertheless, the swell, as predicted by Model B, remained too low for the PS melt of this study and the range of De numbers examined ($h/H = 1.77$ for $De = 5.47$).

Figure 8 shows the various predictions of extrudate swell as a function of De obtained from different models. The experimental data of Huang and White (16) are also presented. Model A follows closely the experimental points up to $De = 2.0$ ($\dot{\gamma}_w = 24$ s $^{-1}$ or $\tau_w = 0.0435$ MPa), but for higher values of De the swell ratio increases much more rapidly than the experimental points. According to Huang and White (16) for $\dot{\gamma}_w > 20$ s $^{-1}$ (or $\tau_w > 0.040$ MPa), the normal stresses obey the following relation

$$N_1 = 1.40 \times 10^{-3} \tau_w^{2.18} \text{ (Pa)} \quad (45)$$

Inclusion of the above relation in Model A for $\dot{\gamma}_w > 20$ s $^{-1}$ brings the swell down and also increases the Deborah number for stability (curve of Model A*). The agreement is therefore largely improved. This change also shows the sensitivity of the results to the various correlations of normal stress data assumed. On the other hand, Model B shows a completely different behavior and the swell increase remains modest even for much higher De numbers than Model A. From these results it is apparent that the elongational viscosity mitigates the effect of the normal stress, which is responsible for the high swelling ratios exhibited by polymer melts. The predictions of the Oldroyd-B model (Crochet and Keunings (6)) lie below both the experimental data and the results obtained with Model A and A*.

The shape of the free surface for the different De numbers examined with Model A is shown in Fig. 9. Some typical velocity profiles and streamline patterns in the vicinity of the exit are shown in Figs. 10 and 11. There is a rearrangement of the profiles

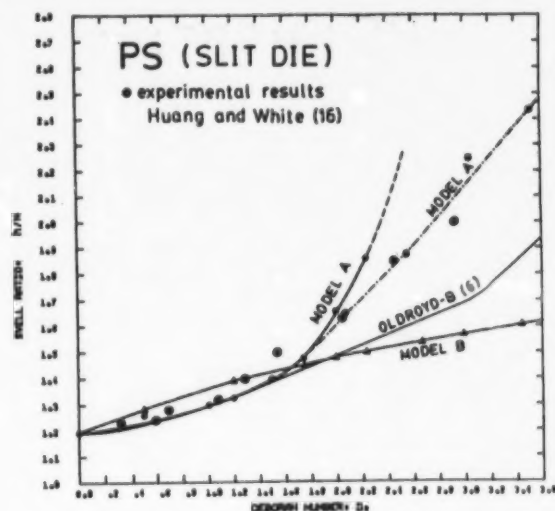


Fig. 8. Extrudate swell versus Deborah number for a PS melt. Predictions from various models and experimental data.

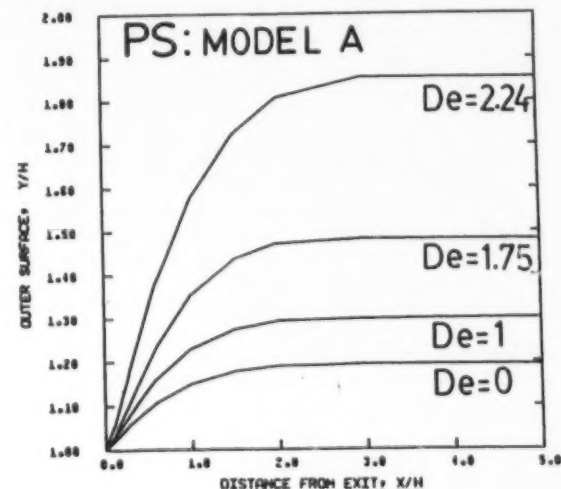


Fig. 9. Shape of the free surface for various De numbers (PS melt, Model A).

as the fluid approaches the exit plane. There is also a small contraction of the streamlines. Actually, the streamline contraction is more pronounced for constant shear viscosity fluids exhibiting quadratic normal stresses (see Mitsoulis [3]) than for shear-thinning fluids with normal stresses. This can be seen in Fig. 12. The corresponding velocity profiles are shown in Fig. 13. From these figures the slight differences in the surface shape may also be noted. The centerline (maximum) velocity exhibits overshoots near the exit plane (Fig. 14). Again these overshoots are more pronounced for the constant shear viscosity fluid. Velocity overshoots of about the same magnitude were also noted by Crochet and Keunings (6) for the Oldroyd-B model. The pressure along the centerline and along the wall is shown in Fig. 15. Discontinuities appear just before the exit plane due to the singularity. Similar discontinuities were also noted by Crochet and Keunings

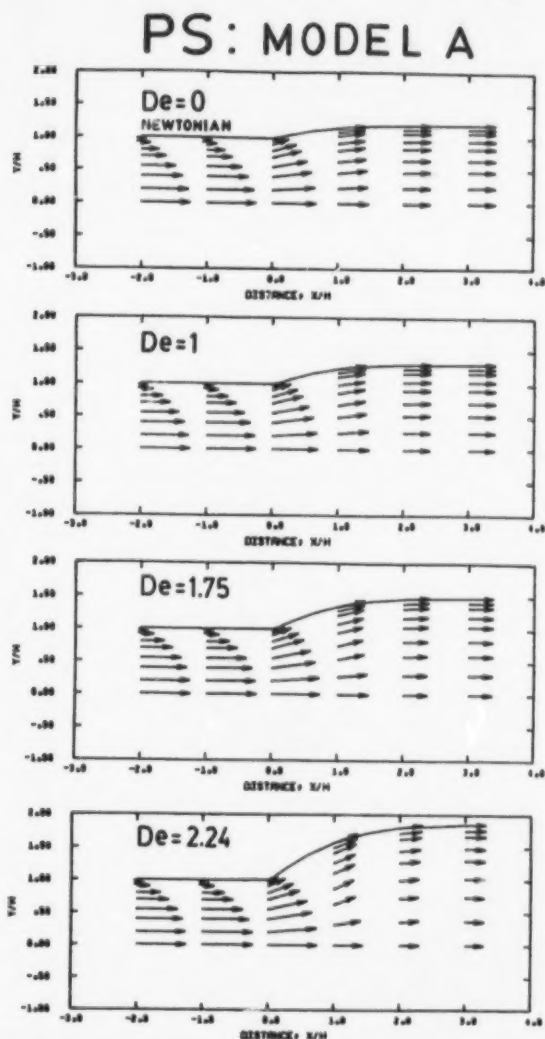


Fig. 10. Velocity fields for various De numbers in die exit flow (PS melt, Model A).

(6) and Caswell and Viriyayuthakorn (19). The results obtained with Model B exhibit the following features: no overshoots are observed in the center-line velocities, the pressure singularities at the exit wall are more pronounced, and the extrudates tend to acquire their final swelling values farther downstream than with Model A.

The pressure drops can be used to calculate the exit pressure loss (exit correction) n_{ex} , which is defined by

$$n_{ex} = \frac{\Delta P - \Delta P_{\infty}}{2\tau_w} \quad (46)$$

where ΔP is the overall pressure drop, ΔP_{∞} is the pressure drop for fully developed flow in the slit without considering the extrudate, and τ_w is the shear stress at the slit wall. Figure 16 shows the model predictions for n_{ex} as a function of De . The second-order fluid asymptote as calculated by Reddy and Tanner (20) is also given along with results obtained from Model A with constant η and

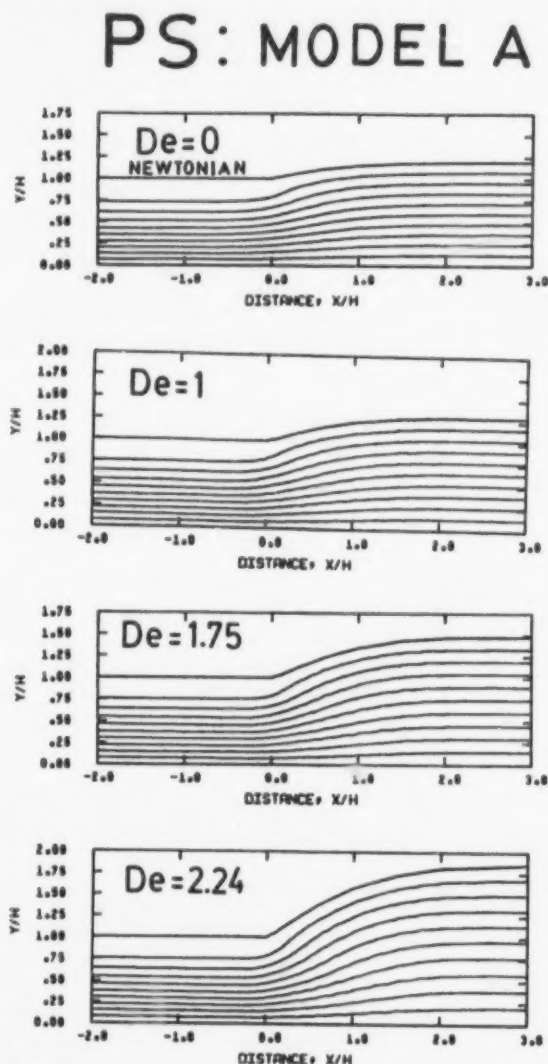


Fig. 11. Streamline patterns for various De numbers in die exit flow (PS melt, Model A).

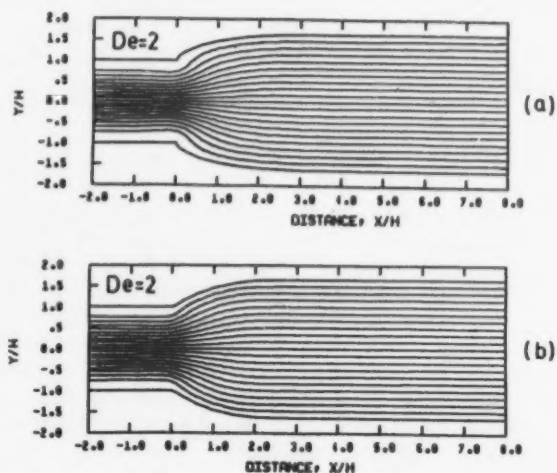


Fig. 12. Streamline pattern for (a) a fluid with a constant viscosity η and quadratic normal stresses $N_1 = \Psi_1 Y^2$ ($\eta, \Psi_1 = \text{const}$); (b) a PS melt ($\eta(Y), \Psi_1(Y)$).

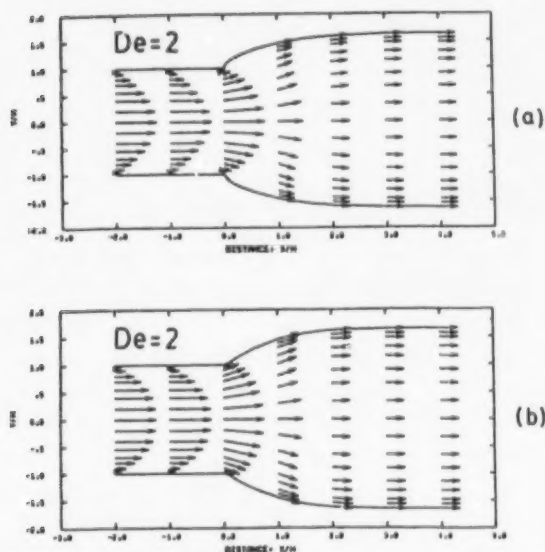


Fig. 13. Velocity fields for (a) a fluid with a constant viscosity η and quadratic normal stresses $N_1 = \Psi_1 \dot{\gamma}^2$ ($\eta, \Psi_1 = \text{const.}$); (b) a PS melt ($\eta(\dot{\gamma}), \Psi_1(\dot{\gamma})$).

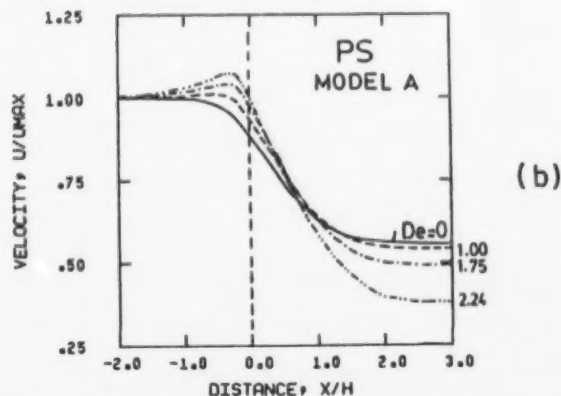
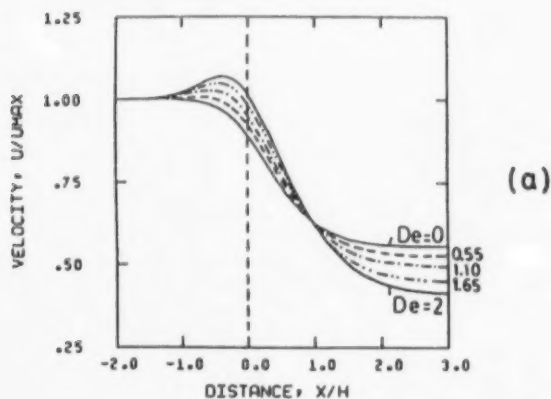


Fig. 14. Centerline velocity for various De numbers (a) fluid with a constant viscosity η and quadratic normal stresses $N_1 = \Psi_1 \dot{\gamma}^2$ ($\eta, \Psi_1 = \text{const.}$); (b) PS melt ($\eta(\dot{\gamma}), \Psi_1(\dot{\gamma})$).

Ψ_1 (3). It should be noted that the second-order fluid has a constant viscosity η and exhibits quad-

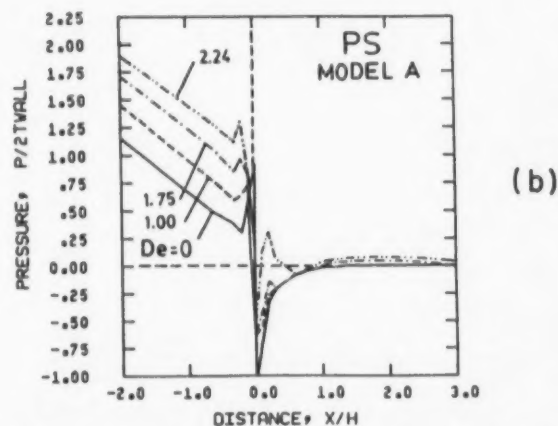
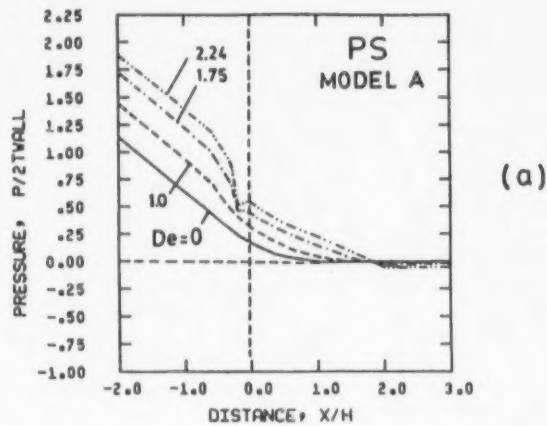


Fig. 15. Pressure distributions for different De numbers in die exit flow (a) centerline pressure, (b) wall/free surface pressure (PS melt, Model A).

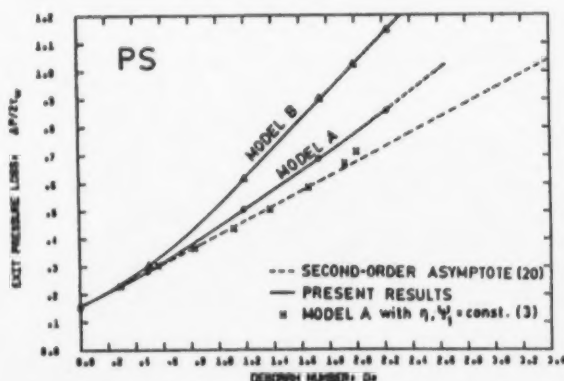


Fig. 16. Exit correction versus Deborah number as predicted by various models.

ratic normal stresses $N_1 = \Psi_1 \dot{\gamma}^2$ in shear flow. While shear-thinning fluids have exit correction values slightly smaller than Newtonian fluids (4), combination of shear-thinning and elasticity increases the exit correction above the second-order values. From the two models, Model B exhibits a higher exit correction than Model A for the same De . This

leads us to the conclusion that the effect of the elongational viscosity as introduced through the present models is to increase the exit correction.

The numerical results for the exit correction from the present simulations, along with the results for the entrance correction for the PS melt, are presented in Table 3 for different De numbers. The sum of entrance and exit correction gives rise to the end (or Bagley) correction n_B . A plot of n_B versus De is presented in Fig. 17. Model A predicts a modest increase for values of De up to 2.24, but then we expect a decrease since the entrance correction decreases rapidly. On the other hand, Model B predicts an almost linear increase of n_B with De that reaches the value of about 4 for $De \approx 5.5$. This trend is in agreement with general observations on polymer melts (5). Nevertheless, the results of Table 3 suggest that the elevated n_B values are due primarily to the exit correction which accounts for about 70 percent of n_B . This is contrary to experimental findings that show the entrance correction to be about 70 to 80 percent of n_B (Choplin and Carreau [18]). Obviously, the discrepancies must be attributed to inadequacies inherent in the present simple models, especially in the case of the entry flow problem where all models have failed to predict a large positive entrance correction.

CONCLUDING REMARKS

A general-purpose finite element program has been used to study the flow of a typical polystyrene melt in the entry region to a die, the flow at the exit, and the accompanying phenomenon of extrudate swell from slit dies. The effects of shear viscosity and normal stresses were examined by means of a simplified constitutive model that is valid in simple shear flow. Although the model is not a general rheological equation of state, it is used as an approximation for these particular problems under the reasoning that there is a preferential direction of flow in both the entry and exit section of a die. Such simplified equations were found to enjoy a wider convergence range than viscoelastic models that obey the principles of tensorial invariance and objectivity.

When the power-law equation for viscosity is used, the present model predicts vortex size, vortex intensity, and extrudate swell not very different from those for purely viscous fluids. This is apparently due to unrealistically high viscosities obtained

from the power-law model for low shear rates. When the viscosity is given by the Carreau relation our model predicts considerable vortex growth at the entry region and extrudate swell at the exit in qualitative agreement with experimental data for polystyrene. While the normal stress is responsible for swelling and exit pressure increase, it causes a reduction of the entrance correction.

The effect of elongational viscosity was studied by allowing the viscosity in the normal stress expressions to be different from that in the shear stress. It was found that the elongational viscosity is responsible for the well-known increase of entrance correction with the Deborah number (stress ratio). On the other hand, the elongational viscosity mitigates the effect of normal stresses on the swelling at the exit.

Neither one of the two versions of the present model is a general constitutive equation because they do not satisfy the principles of tensorial invariance and objectivity. In fact the model is not even symmetric, which means that it can be applied only for flow problems where a dominant flow direction can be unambiguously identified. This model does not include memory effects because the stresses are related to the local values of the rate-of-strain ten-

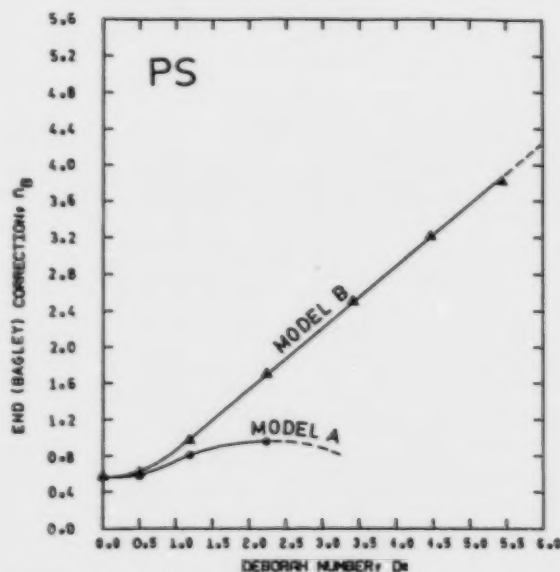


Fig. 17. End (Bagley) correction versus Deborah number as predicted by Models A and B (PS melt).

Table 3. Entrance, Exit, and End (Bagley) Correction for Different De Numbers as Predicted by Model A and B for the Flow of a PS Melt Through a Slit Die.

De	$\dot{\gamma}_w (s^{-1})$	$\tau_w (MPa)$	Model A			Model B		
			n_{en}	n_{ex}	n_B	n_{en}	n_{ex}	n_B
0.0	(all $\dot{\gamma}$)	(all τ)	0.407	0.153	0.560	0.407	0.153	0.560
0.5	0.60	0.0052	0.300	0.287	0.587	0.305	0.302	0.607
1.2	5.15	0.0200	0.283	0.516	0.799	0.355	0.617	0.972
2.24	34.06	0.0518	0.086	0.866	0.952	0.571	1.153	1.724
3.46	126.80	0.1000	-0.300	~(1.025)	~(0.725)	0.772	1.747	2.519
4.52	285.18	0.1500	-0.618	—	—	0.980	2.246	3.226
5.47	506.84	0.2000	-1.003	—	—	1.154	2.684	3.838

sor. Nevertheless the predictions have a striking similarity to other numerical calculations involving well-accepted constitutive equations. This is an indication that the terms required in the extra stress tensor for tensorial invariance and objectivity do not contribute much to the solution while they may accelerate the breakdown of the numerical schemes. The present model allows the introduction of experimentally measured shear viscosity, elongational viscosity, and normal stresses so that direct comparisons can be made with experimental observations on polymer melt flows.

ACKNOWLEDGMENTS

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NOMENCLATURE

A	= Constant in power-law Eq 11, Pa^{1-b} .
$[B]$	= Rate-of-strain matrix.
b	= Exponent in power-law Eq 11, dimensionless.
b_i	= Body force, N .
$[D]$	= Constitutive matrix.
De	= Deborah number, Eq 13, dimensionless.
$\{F\}$	= Force vector, N .
H	= Half die gap, cm .
h	= Half extrudate thickness, cm .
$\{I\}$	= Vector containing the Kronecker deltas.
I_2	= Second invariant of the rate-of-strain tensor, s^{-2} .
$[K]$	= Stiffness matrix.
m	= Consistency index, $\text{Pa}\cdot\text{s}^m$.
N	= Interpolation function, dimensionless.
N_1	= First normal stress difference, Pa .
N_2	= Second normal stress difference, Pa .
n	= Power-law index, dimensionless.
n_B	= End (Bagley) correction, dimensionless.
n_{en}	= Entrance correction, dimensionless.
n_{ex}	= Exit correction, dimensionless.
p	= Pressure, Pa .
Re	= Reynolds number, dimensionless.
r	= Radial coordinate, cm .
$[S]$	= Stream function stiffness matrix.
S_R	= Stress ratio, Eq 13, dimensionless.
T	= Surface traction, N/cm^2 .
u	= Velocity in x-direction, cm/s , velocity in r-direction, cm/s .
v	= Velocity in y-direction, cm/s .
v_x	= Velocity in x-direction, cm/s .
v_y	= Velocity in y-direction, cm/s .
w	= Velocity in z-direction, cm/s .
W_s	= Weissenberg number, dimensionless.
$\{X^*\}$	= Vector of nodal unknowns.
z	= Axial coordinate, cm .
Γ_i	= Boundary surface with specified tractions, cm^2 .
$\dot{\gamma}$	= Rate-of-strain, s^{-1} .
$\dot{\gamma}_w$	= Wall shear rate, s^{-1} .

ΔP	= Total pressure drop, Pa .
ΔP_{res}	= Pressure drop in reservoir for fully developed flow, Pa .
ΔP_{sl}	= Pressure drop in the slit for fully developed flow, Pa .
δ	= Denotes virtual (arbitrary) change.
δ_{ij}	= Kronecker delta, dimensionless.
$\dot{\epsilon}$	= Half rate-of-strain, s^{-1} , elongational rate, s^{-1} .
η	= Viscosity, $\text{Pa}\cdot\text{s}$.
η_0	= Zero-shear viscosity, $\text{Pa}\cdot\text{s}$.
η_T	= Elongational viscosity, $\text{Pa}\cdot\text{s}$.
θ	= Angle measured around the z-axis (cylindrical coordinates).
λ	= Time constant, s .
σ	= Total stress, Pa .
τ	= Extra stress, Pa .
τ_0	= Extra stress due to normal forces, Pa .
τ_w	= Wall shear stress, Pa .
Ψ_1	= First normal stress coefficient, $\text{Pa}\cdot\text{s}^2$.
Ψ_2	= Second normal stress coefficient, $\text{Pa}\cdot\text{s}^2$.
Ψ	= Stream function, cm^2/s .
Ω	= Volume, cm^3 .
ω	= Vorticity, s^{-1} .

REFERENCES

1. M. J. Crochet and K. Walters, *Ann. Rev. Fluid Mech.*, **15**, 241 (1983).
2. E. Mitsoulis, J. Vlachopoulos, and F. A. Mirza, *Polym. Proc. Eng.*, **1**, 281 (1983).
3. E. Mitsoulis, Ph.D. Thesis, Dept. Chem. Eng., McMaster Univ., Hamilton, Ontario (1984).
4. E. Mitsoulis, J. Vlachopoulos, and F. A. Mirza, *Polym. Eng. Sci.*, **24**, 707 (1984).
5. J. L. White, *Appl. Polym. Symp.*, **20**, 155 (1973).
6. M. J. Crochet and R. Keunings, *J. Non-Newt. Fluid Mech.*, **10**, 339 (1982).
7. R. Keunings and M. J. Crochet, *J. Non-Newt. Fluid Mech.*, **14**, 279 (1984).
8. R. B. Bird, R. C. Armstrong, and O. Hassager, "Dynamics of Polymeric Liquids," Vol. I, J. Wiley, New York (1977).
9. K. Oda, J. L. White, and E. S. Clark, *Polym. Eng. Sci.*, **18**, 25 (1978).
10. C. D. Han, Y. J. Kim, and H.-K. Chuang, *Polym. Eng. Reviews*, **3**, 1 (1983).
11. M. Takahashi, T. Masuda, and S. Onogi, *J. Soc. Rheol. Jpn.*, **11**, 13 (1983).
12. H. C. Martin and G. F. Carey, "Introduction to Finite Element Analysis," McGraw-Hill, New York (1973).
13. E. Mitsoulis, J. Vlachopoulos, and F. A. Mirza, "MACVIP—A Finite Element Program for Creeping Viscoelastic Flows," Internal Report, Faculty of Engineering, McMaster University, Hamilton, Ontario (1983).
14. J. L. White and A. Kondo, *J. Non-Newt. Fluid Mech.*, **3**, 41 (1977).
15. E. B. Bagley and H. P. Schreiber, "Rheology, Vol. 5," ed. F. R. Eirich, p. 93, Academic Press, New York (1969).
16. D. C. Huang and J. L. White, *Polym. Eng. Sci.*, **19**, 609 (1979).
17. H. Nguyen and D. V. Boger, *J. Non-Newt. Fluid Mech.*, **5**, 353 (1979).
18. L. Choplin and P. J. Carreau, *J. Non-Newt. Fluid Mech.*, **9**, 119, (1981).
19. B. Caswell and M. Viriyayuthakorn, *J. Non-Newt. Fluid Mech.*, **12**, 13 (1983).
20. K. R. Reddy and R. I. Tanner, *J. Rheol.*, **22**, 661 (1978).

Melt Rheology and Extrudability of Polyethylenes

L. A. UTRACKI and A. M. CATANI

Industrial Materials Research Institute
National Research Council of Canada
75, boul. de Mortagne
Boucherville, Québec J4B 6Y4

Commercial high density polyethylene (HDPE), low density polyethylene (LDPE), and linear low density polyethylene (LLDPE) resins were tested at 150, 170, and 190°C in steady state, dynamic, and extensional modes. Within the low rates of deformation $\dot{\gamma} = \omega \leq 0.3$, the steady state and dynamic functions agreed: $\eta = \eta'$ and $N_1 = 2G'$; at the higher rates, the steady state parameters were larger. The elongational viscosity, η_e , was measured under a constant rate, $\dot{\epsilon}$, or stress, σ , condition. In the first case for LLDPE, the transient η'_e reached an equilibrium plateau value, η_e . For HDPE, η'_e increased up to the break point. For LDPE, stress hardening was recorded. Under constant stress the η_e could always be determined; its value, within experimental error, agreed with the maximum value of η'_e determined in a constant $\dot{\epsilon}$ experiment. The maximum strain at break was only $\epsilon = 1.5$ for HDPE and 3 to 4 for LDPE and LLDPE. The rate of deformation dependence of the η (or η') and η_e may be discussed in terms of the Trouton ratio, $R_T = \eta_e/3\eta$ at $\dot{\gamma} = \omega = \dot{\epsilon}$: $R_T \leq 1.2$ for LLDPE, $R_T \leq 2.5$ for HDPE, and $R_T \leq 15$ for LDPE. The PE resins were extruded at 190°C through a laboratory extruder equipped with a slit or rod die. The rotational speed of the screw varied from 0 to 90 rpm. Extrusion pressure, output, and energy were measured and correlated with the rheological parameters of the resins.

INTRODUCTION

This is a second part of the work on the relation between the rheology and processability of polyethylenes. In the first part (1) we concentrated on the melt rheology and relative behavior of these resins in the liquid state. Special attention was given to the extensional flow. In spite of a fair number of publications on the subject (2 to 6), the importance of elongational flow in plastics processing has not been adequately realized by the industry. In this paper the correlation between dynamic, shear, and uniaxial extensional viscosities of commercial polyethylenes and their extrudability is examined.

EXPERIMENTAL

Four commercial polyethylene (PE) samples: linear low density (LLDPE), high density (HDPE), and a low density (LDPE), resins, supplied through the courtesy of Union Carbide Canada Ltd., were used. Their properties are listed in Table 1.

The shear properties of the samples at 150, 170, and 190°C were determined in dynamic and rotational modes using the Rheometrics Mechanical Spectrometer (RMS), Model 605. For each sample at each temperature, first the strain, γ , and time, t ,

sweep tests, at two frequencies $\omega = 0.1$ and 10 (rads/s), were done. In all cases, the linear viscoelastic region of γ , measured over a period of stable response, was found. The flow at a high range of $\dot{\gamma}$ was studied using the Instron Capillary Rheometer (ICR), Model 3211. The Rabinowitsch and Bagley corrections were used. It was found that in some cases die slip occurred (e.g. low temperature extrusion of LLDPE) and the Mooney correction had to be applied (7 to 9).

Elongational properties were determined in the Rheometrics Extensional Rheometer (RER). The instrument, described in the literature (10 to 12), was used in constant elongation rate, $\dot{\epsilon}$, and constant extensional stress, σ_{11} , modes. The samples were transfer molded under vacuum, annealed, and then affixed to the aluminum ties. The initial length and diameter of the samples were, respectively: $L_0 = 21.0 \pm 0.5$ and $D_0 = 5.54 \pm 0.05$ mm. In order to determine the effect of the residence time, t_R , the samples were evaluated in RER for up to 30 min, and tested for weight gain/loss after exposure to silicon oil for up to 23 h (14, 15).

The molecular parameters of the samples were determined by gel permeation chromatography using a Waters Sci. GPC-150C instrument at 135°C

Table 1. Properties of Polyethylene Resins.

N°	CODE	Density ^a ρ (kg/m ³)	Melt Index ^b (g/10')		10 ⁻³ × Molecular Weights ^c		
			Nominal	Measured	M _n	M _w	M _z
1	LLDPE	918	1.0	0.71	97.5	261	624
2	HDPE	953	0.2	0.20	43.5	306	1021
3	LDPE-1	921	0.15	0.14	55.6	264	625
4	LDPE-2	922	5.5	4.06	39.1	210	668

Notes: (a) ρ at 150 and 190°C was calculated (13) as 781 and 751 kg/m³, respectively; (b) MI at 190°C with 2100 g; and (c) by GPC at 135°C in TCB.

with 1,2,4-trichlorobenzene (TCB) as a solvent. The four columns (10³, 10⁴, 10⁵, and 10⁶ Å) were calibrated using 24 polystyrene standard samples. The results are listed in Table 1. To prevent oxidative degradation of PE, 0.1 weight-percent of antioxidant (Topanol CA, Nonox DLTDP; 50:50) was added. There was no change in GPC traces for samples molded and sheared on RMS for 45 min at 190°C (16, 17).

PE resins (as received) were extruded through a 19-mm-diameter laboratory extruder attachment to the Brabender Plastograph Model EPL-V5501. Screw N° 043-3 (diameter $D = 19.01$ mm, length $L = 25D$, helix angle $\phi = 17.66^\circ$, channel depth $h = 1.778$ mm, rib width $E = 3.175$ mm, flight clearance $\delta = 0.061$ mm, and a compression ratio of 2.90) and commercial slit and rod dies were used. Their dimensions were, respectively: width $w_s = 76.04$, length $l_s = 25.14$, thickness $h_s = 0.52$ mm; and diameter $d = 5.80$, $l = 43.07$ mm. The pelletized HDPE and LDPE resins were fed by gravity while the granules of LLDPE were fed by means of a force-feeder.

RESULTS

The extensional behavior of the PE resins were previously discussed (1, 14). Note that both constant stress and constant strain rate type measurements were superimposable. The stress growth function, η'_s , in elongation and in steady state shearing correlated quite well. As expected, η'_s versus time, t , shows strain hardening for LDPE, continuous growth for $t \leq 10^3$ sec for HDPE and a very flat response ($\eta'_s \approx 10^5$ Pa.s) at $1 \leq t \leq 10^3$ for LLDPE. Plotting η' versus ω and $\eta_s/3$ versus $\dot{\epsilon}$ at $T = \text{const}$, the following results were obtained: for HDPE and LLDPE, the two functions were similar, the largest difference for HDPE was observed at the lowest temperature—in this case $R_T = \eta_s/3\eta'$ at $\dot{\epsilon} = \omega$ was about 2.5, for LLDPE $R_T \leq 1.2$; for LDPE, the two functions were quite different; while η' is a monotonically decreasing function of ω , the η_s passes through a maximum at high rates of deformation and at lower temperatures; the strain-hardened LDPE had $R_T = 10$ to 15.

The four polyethylene resins listed in Table 1 were extruded using a programmed temperature profile to assure 190°C at the die. A screw speed of $N = 0$ to 90 rpm was used. To evaluate the performance, the extrusion was carried out without a die (but with a breaker plate and a screen pack), and with two dies for rod and slit extrudates. The

output, Q (g/min), die pressure, ΔP (MPa), and torque, c (Nm) were measured.

The reduced output rate, $\dot{Q} = Q/N$ (in grams) vs. screw speed, N (rpm), is shown in Fig. 1. There are three distinct groups of points: the upper, for extrusion without a die where the drag flow determines the output; the middle one, for extrusion of rod; and the bottom one, for extrusion through a slit die. Rejecting the lowest and the highest speed data at $N = 10$ and 90 rpm, the calculated average values at $\dot{Q}$ are listed in Table 2. The values for LLDPE and the low molecular weight LDPE-2 are higher than those for HDPE and LDPE-1. These effects may be explained in terms of differences in the feeding method, the melting behavior, the screw design, and the solid-solid friction coefficient. The combined theories of Darnell and Mol (18) and Chung (19) may be used as a basis for discussion.

In Fig. 2, the increase of die pressure, ΔP , as a function of N is shown; the onset of sharkskin is also indicated.

In Figs. 3 and 4, the standard characteristic plot for the extruder: Q versus ΔP for the four resins is shown. In the figures, the vertical lines indicate Q variation with ΔP for a given die (the data points for extrusions without a die are on the Y-axis), whereas the horizontal ones that dependence for $N = \text{const}$.

In Figs. 5 and 6, the measure of the energy consumption per unit of output:

$$Z = (c - c_0)/Q$$

is shown as a function of P for the four resins. In this relation, c_0 and c stand for torque of the empty and full extruder, respectively. The Y-axis shows the data for runs without a die, and away from it, those for runs with rod and slit dies. It can be seen that efficiency improves with N . The highest Z are obtained for LLDPE, then sequentially for HDPE, LDPE-1, and LDPE-2. This sequence is no surprise to processors. It has been known that it is easier to extrude LDPE than HDPE and/or LLDPE. However, our results for these two latter resins (note that their η 's at the extrusion speeds are comparable) indicate that, systematically, Z for LLDPE is larger than for HDPE.

In the previous comparative studies (20, 21) of industrial extrusion of PE's, the processing conditions were adjusted for each resin, e.g. changing T from 170°C for LDPE to 230°C for LLDPE. Only under these variable conditions can the blown film extrusion of HDPE be found to exhibit higher torque and die pressure, followed by LLDPE and, lastly, conventional LDPE.

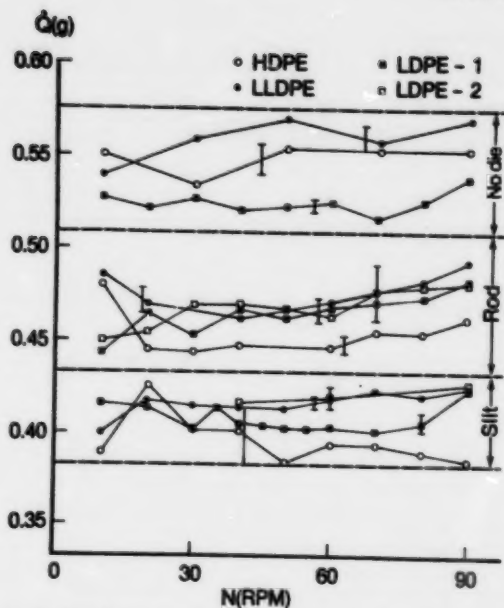


Fig. 1. Reduced output rate $\dot{Q} = Q/N$ versus N for the four PE resins extruded without a die (top), through a rod die (middle), and through a slit die.

Table 2. The Average Output Rates for Polyethylenes.

No.	Resin	$\dot{Q}$ (g)		
		No die	Rod die	Slit die
1	LLDPE	0.560 ± 0.013	0.472 ± 0.007	0.417 ± 0.003
2	HDPE	0.548 ± 0.008	0.448 ± 0.005	0.398 ± 0.015
3	LDPE-1	0.523 ± 0.003	0.467 ± 0.007	0.407 ± 0.005
4	LDPE-2	—	0.477 ± 0.015	0.420 ± 0.005

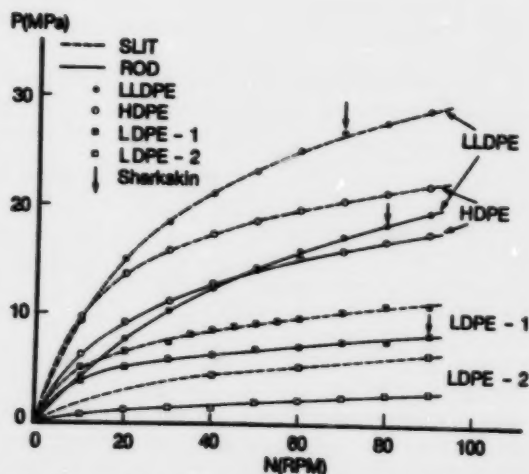


Fig. 2. Die pressure versus N for the PE resins extruded through rod (solid line) and slit (broken line) dies. The onset of surface roughness is indicated.

DISCUSSION AND CONCLUSIONS

Rheological Observations and Correlations

The steady and dynamic shear and elongational flow properties of four PE resins were determined. A number of observations are worth recalling:

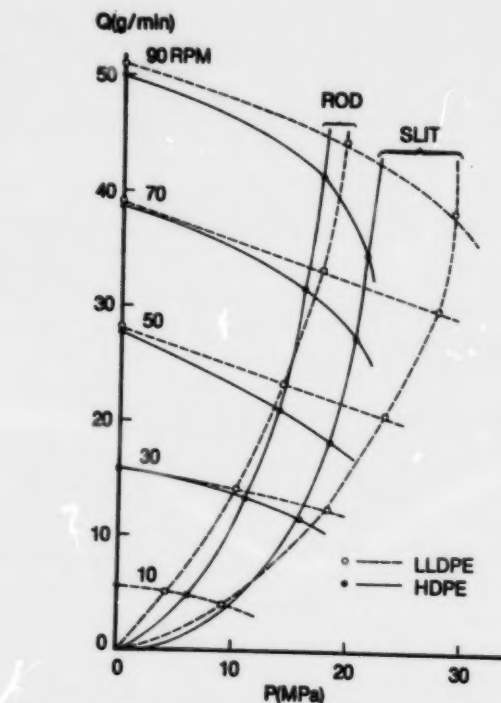


Fig. 3. Q versus P plot for LLDPE and HDPE extruded without a die and through rod and slit dies at $N = \text{const}$.

- The equilibrium elongational viscosity, η_e , defined as a maximum and/or plateau value of η'_e for constant $\dot{\epsilon}$ experiments agrees well with its analog calculated from the strain slope in a constant σ_{11} experiment.
- At vanishingly small rates of deformation:

$$\lim \eta = \lim \eta' = \lim \eta_e/3$$

$$\dot{\gamma} \rightarrow 0 \quad \omega \rightarrow 0 \quad \dot{\epsilon} \rightarrow 0$$

- The maximum value of R_T was the lowest for LLDPE (value of 1.2) and the highest for LDPE (value of 15), with HDPE (value of 2.5) in between.
- At low rates of deformation: $\eta = \eta'$ and $N_1 = 2G'$ (ref. 14). At rates above about 10 (rad/s): $\eta \approx \eta''$ and $N_1 > 2G'$ (ref. 9) were found.
- The maximum strain at break: $\epsilon_c = 1.5$ for HDPE and $\epsilon_c > 3$ for LLDPE and LDPE.
- For LDPE the function $\eta_2/3 = f(\dot{\epsilon}, T)$, determined in the extensional experiment, may be used as an estimate for $\eta = f(\dot{\gamma}, T)$ at $\dot{\epsilon} = \dot{\gamma}$.

Analysis of the Extrusion

During normal operation, the extruder output is controlled by the pumping capacity of the metering zone (22). For small extruders with relatively low rotational screw speed ($N < 90$ rpm) isothermal conditions are generally adopted. Under these conditions, for a square pitch screw, Q can be expressed as

$$Q = Q/N = \alpha - \beta (\partial P / \partial L) / N \eta, \quad (1)$$

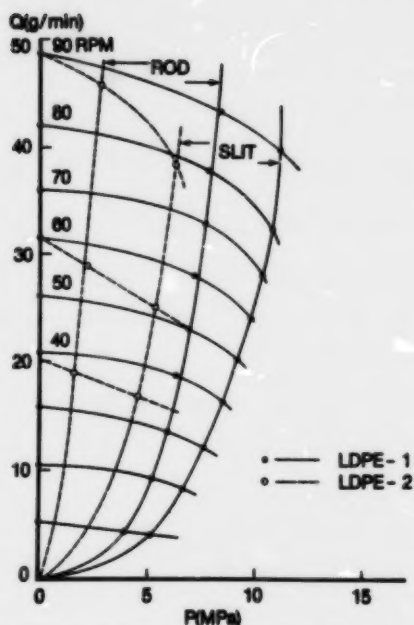


Fig. 4. Q versus P plot for LDPE-1 and LDPE-2 extruded without a die and through rod and slit dies at $N = \text{const.}$

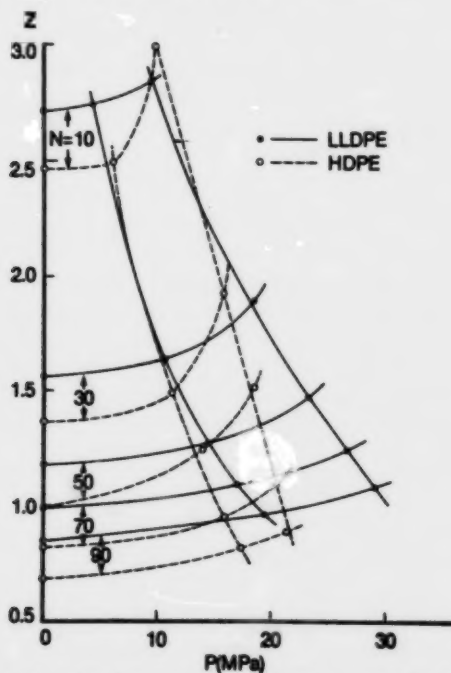


Fig. 5. The reduced energy consumption Z versus P for LLDPE and HDPE extruded without a die and through rod and slit dies at $N = \text{const.}$

where

$$\alpha = 1.4263 D^2 h (1 - E/D) (1 - \delta/h) \rho F_d \quad (2)$$

$$\beta = 0.0241 D h^3 (1 - E/D) \rho F_p \quad (3)$$

In Eqs 1 to 3, η is the "back flow" viscosity in the barrel calculated at the average rate of shear in the screw channel:

$$\dot{\gamma}_B = \pi D N / h \quad (4)$$

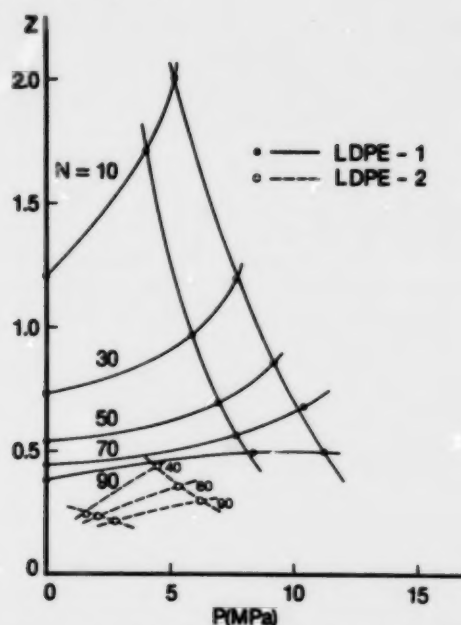


Fig. 6. The reduced energy consumption Z versus P for LDPE-1 and LDPE-2 extruded without a die and through rod and slit dies at $N = \text{const.}$

F_d and F_p are the "shape factors" for drag and pressure flows determined by the h/w - ratio; for the extruder used in this study, $F_d = 0.93$ and $F_p = 0.92$ were determined (22). It is worth noting that in Eq 2 the leakage flow was also taken into account. Substituting the numerical values, one finds:

$$\alpha = 0.515 \text{ g}$$

$$\beta = 1.48 \times 10^{-4} \text{ g} \cdot \text{cm}$$

Assuming uniform pressure gradient along the screw and taking the experimental values of η (determined for these resins in ICR) appropriate for each $\dot{\gamma}_B$, the broken lines shown in Fig. 7 were computed. It can be seen that at low N and low P the agreement with the experimental values is good. For extrusions without a die ($P = 0$) at increasing N , the output becomes progressively larger than computed. The reason for this is probably due to an increase of melt density as a result of increased pressure and/or decreased temperature in the metering zone; $\rho = 751 \text{ (kg/m}^3\text{)}$ computed for $P = 0$ and $T = 190^\circ\text{C}$ has been used in these calculations. The second deviation from the predictions of Eq 1 concerns the pressure dependence of Q for $N = \text{const.}$

It is obvious that the experimentally found decrease of Q upon increase of P is larger than computed. The reasons for this may be nonisothermal conditions, large pressure drop across the screen packs, or the rheological effects not considered in the derivation of Eq 1. As reported in Table 3, the constant stress values of η , and G' as well as the extrudate swell increase in the same sequence as the magnitude of the slope deviation: LLDPE, HDPE, LDPE-1. It should also be noted that much better agreement can be obtained with the experi-

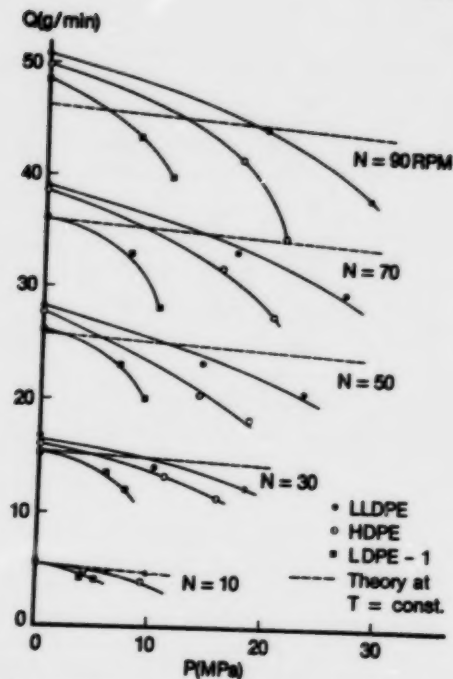


Fig. 7. Comparison between the experimental Q versus P dependencies (solid lines) for LLDPE, HDPE, and LDPE-1 extruded without a die and through rod and slit (higher and lower output resp.) dies at $N = \text{const.}$

Table 3. Measured Properties of PE Resins at 190°C.

No.	Property	LLDPE No. 1	HDPE No. 2	LDPE-1 No. 3	LDPE-2 No. 4
1	c; rod/slit die	42/41	34/13	23/22	13/11
2	P; rod/slit die	25/17	21/16	10/7.6	6.0/2.6
3	Bulk density (g/L)	452	623	568	565
4	$\eta_0 \times 10^{-3}$	8.9	127	197	4.97
5	$\eta_{0.0} \times 10^{-3}$	(37.7)	490	660	16
6	η	2660	2340	744	176
7	η_a (at $\sigma_{11} = 10^4$)	(36.0)	360	2000	4.5
8	$G' \times 10^{-3}$ (Pa)	45.8	75.8	88.6	0.846
9	$G'' \times 10^{-3}$ (Pa)	1597	37.7	6.3	15.4
10	ω_c (rad/sec)	2981	6.3	0.25	39.6
11	ϵ_c	3.0	1.5	>3.5	3.5
12	% extrudate swell ($l/d = 1$) rod die	50	70	124	5

Notes: Torque, $c(N \cdot m)$ at 70 rpm; pressure P (MPa) at 70 rpm; η_0 , $\eta_{0.0}$ = zero deformation rate, shear, η , and elongational viscosity, η_a (Pa.s); η_0 and $\eta_{0.0}$ in parentheses calculated from 190°C results using the activation energy of flow $E_a = 34.95$ (kJ/mole); G' , η and η_a taken at constant stress $\sigma_{12} = 10^4$ and $\sigma_{11} = 10^4$ Pa, respectively. G' , ω_c define $G' = G''$ condition.

mental data if η in Eq 1 is taken at constant stress instead of constant rate.

Die Flow

The shear viscosity, $\eta = \sigma_{12}/\dot{\gamma}$, can be determined from the capillary and slit die flows if the die geometry, output, and pressure drop are known (23). For capillary dies:

$$\sigma_{12} = (P - P_e)/4(l/d) \quad (5)$$

$$\dot{\gamma} = (Q/\pi R^3 \rho) (3 + b) \quad (6)$$

where

$$b = \partial \ln Q / \partial \ln P \quad (7)$$

and P_e is the Bagley entrance/exit pressure drop correction. For slit dies:

$$\sigma_{12} = (P - P_e) h_s/2l_s \quad (8)$$

$$\dot{\gamma} = (2Q/h_s^2 w_s \rho) (2 + b) \quad (9)$$

where h_s , l_s , and w_s represent the slit gap, length, and width, respectively.

As indicated is Eqs 5 to 9 for calculation of the true stress, the P_e has to be determined. In the case of the ICR, using up to nine dies of different l and d , P_e was computed and the true η versus $\dot{\gamma}$ dependence was derived. Such a correction could not be determined for the rod and slit dies. Assuming $P_e = 0$, the apparent viscosities, η_{app} , were computed. On the other hand, the Rabinovitsch correction for $\dot{\gamma}$ was systematically applied. The results of these calculations are shown in Figs. 8 to 11. It is remarkable that excellent agreement is obtained between η and $\eta_{app}(\text{slit})$, whereas large differences are observed between η and $\eta_{app}(\text{rod})$. The reason lies in the geometry; in the first case $l_s/h_s = 48.4$, whereas in the second $l/d = 7.4$. The maximum difference between η and $\eta_{app}(\text{slit})$ of 20 percent was obtained for LDPE-1. (The 20 percent lower $\eta(\text{slit})$ values may indicate disentanglement.) For the rod-die, the entrance/exit correction factor $\sigma_F = (\eta_{app} - \eta) \times \dot{\gamma}$ (Pa) was found to depend on σ_{12} and to follow the same dependence as that determined for the Bagley correction in ICR flow. This was to be expected, since for the nonslip systems P_e versus σ_{12} was found to be independent of the capillary diameter.

On the other hand, there is still the question as

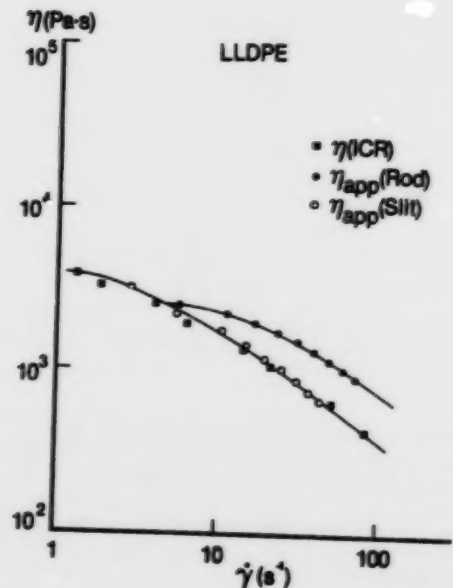
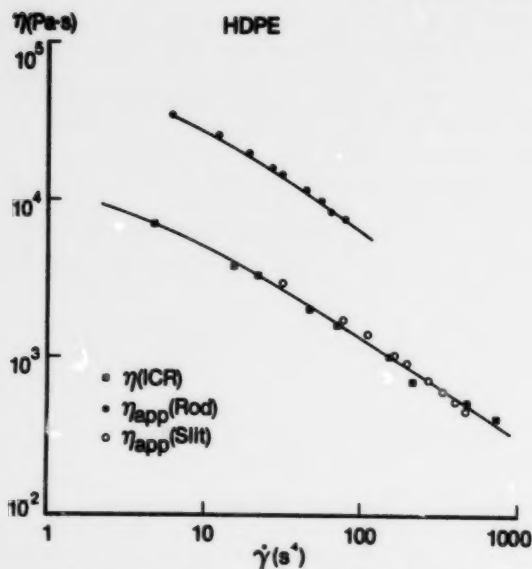
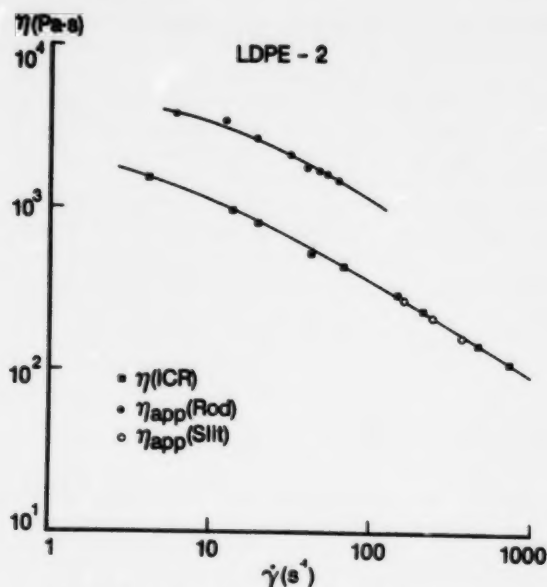
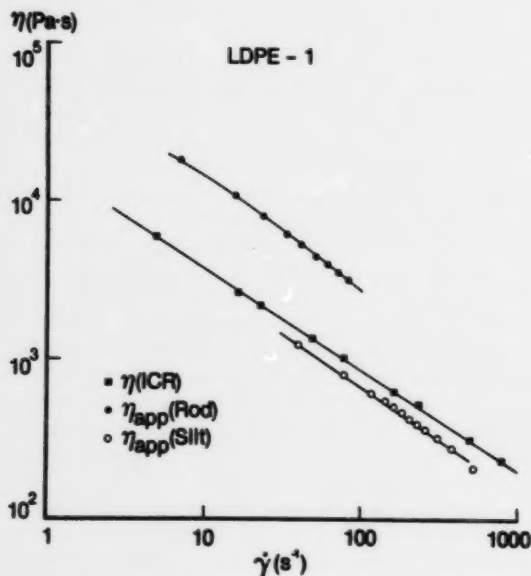


Fig. 8. η and η_{app} versus $\dot{\gamma}$ for LLDPE at 190°C.

Fig. 9. η and η_{app} versus $\dot{\gamma}$ for HDPE at 190°C.Fig. 11. η and η_{app} versus $\dot{\gamma}$ for LDPE-2 at 190°C.Fig. 10. η and η_{app} versus $\dot{\gamma}$ for LDPE-1 at 190°C.

to what material functions determine P_e . From the values quoted in this paper and the careful analysis of data, it is apparent that not only the melt elasticity but also the elongational flow parameters must be taken into account. Mathematical modeling of capillary flow for viscoelastic fluids should allow specific effects to be assigned to each of the components of the stress tensor.

ACKNOWLEDGMENT

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REFERENCES

1. L. A. Utracki, A. Catani, J. Lara, and M. R. Kamal, European Meeting on Polymer Process Prop., 13-16 June 1983, Capri, Italy.
2. C. J. S. Petrie and J. M. Dealy, *Proceed. 8th Intl. Congress on Rheology*, G. Astarita, G. Marrucci, and L. Nicolais (Eds.), Vol. 1, p. 177, Plenum Press, New York (1980).
3. C. F. Denson, *Polym. Eng. Sci.*, **13**, 125 (1973).
4. J. A. Brydson, "Flow Properties of Polymer Melts," G. Godwin Ltd., London, (1981).
5. K. Walters, "Rheometry," Chapman and Hall, London, (1975).
6. Z. Tadmor and C. G. Gogos, "Principles of Polymer Processing," J. Wiley & Sons, New York (1979).
7. L. A. Utracki and M. R. Kamal, *Proceed AICHE meeting*, Los Angeles, CA, November 14-19, 1982 Paper No. 3b.
8. L. A. Utracki and M. M. Dumoulin, *SPE ANTEC Tech. Papers*, **28**, 51 (1982).
9. L. A. Utracki and R. Gendron, *Proceedings Annual Meeting CSChE*, Toronto, 1983; *J. Rheology*, **28**, 601 (1984).
10. H. Munstedt, *J. Rheology*, **23**, 421 (1979).
11. H. M. Laun and H. Munstedt, *Rheologica Acta*, **15**, 517 (1976).
12. V. S. Au-Yeung and C. W. Macosko, *Mod. Plast.*, **58**, 84 (1981); *J. Rheology*, **25**, 455 (1981).
13. O. Olabisi and R. Simha, *Macromolecules*, **8**, 211 (1975).
14. L. A. Utracki and J. Lara, 2nd Intl. Workshop on Extensional Flows, 24-28 January 1983, Mulhouse-La Bresse (France).
15. L. A. Utracki and J. Lara, NRCC-IMRI, mini-symposium "Composites-82," Nov. 30, 1982; *Polym. Compos.*, **5**, 44 (1983).
16. M. M. Dumoulin, L. A. Utracki, and J. Lara, NRCC-IMRI, mini-symposium "Polyblends-83," April 12, 1983; *Polymer Eng. Sci.*, **24**, 117 (1983).
17. L. A. Utracki and M. M. Dumoulin, *ACS Div. Org. Coat. Plastics Chem.*, **48**, 859 (1983); *Polym. Plast. Tech. Eng.*, **23**, 193 (1984).
18. W. H. Darnell and E. A. J. Mol, *SPE J.*, **12**(4) (1956).
19. C. I. Chung, *SPE J.*, **26**(5), 33 (1970).
20. K. Krumm and W. Predol, *SPE ANTEC Tech. Papers*, **28**, 209 (1982).
21. V. H. Karl and W. R. Hofer, *SPE ANTEC Tech. Papers*, **28**, 196 (1982).
22. E. C. Bernhardt, Ed., "Processing of Thermoplastic Materials," R. E. Krieger Publ. Co., Malabar, FL, (1974).
23. J. M. Dealy, "Rheometers for Molten Plastics," Van Nostrand Reinhold Co., New York, (1982).

NOMENCLATURE

PE	= Polyethylene.
HDPE, LDPE and LLDPE	= High density, low density, and linear low density (gas phase) PE, respectively.
b	= Slope, defined by Eq 7.
c_0, c	= Torque of empty and full extruder, respectively ($N \cdot m$).
d	= Diameter of the capillary (mm).
D	= Diameter of extruder barrel.
D_0	= Diameter of premolded sample for elongational testing.
E	= Extruder screw rib width.
E_a	= Activation energy of flow (kJ/mole).
F_d and F_p	= Shape factors in Eqs 2 and 3, respectively.
G', G''	= Storage and loss shear moduli (Pa).
G_x	= Value of the shear moduli at $G' = G'' = G_x$.
h	= Screw channel depth (mm).
h_s	= Slit gap (mm).
l, l_s	= Length of the capillary and slit-die, respectively (mm).
L	= Length of the extruder screw (mm).
L_0	= Length of premolded sample for elongational testing (mm).
M_n, M_w, M_z	= Number, weight, and z-average molecular weights.
MI	= Melt index (g/10 min).
N	= Screw speed (rpm).
N_1	= First normal stress difference.
P	= Pressure (Pa).
P_e	= Bagley correction in Eqs (5) and (8) (Pa).
ΔP	= Die pressure drop (MPa).
Q	= Output (g/min).
$\bar{Q}$	= Output per single screw revolution (g).
R	= Capillary radius (mm).
R_T	= Trouton ratio ($= \eta_e/3\eta'$).
t	= Time (min).
t_R	= Residence time (min).
T	= Temperature ($^{\circ}\text{C}$).
w_s	= Slit width.
Z	= Energy consumption per unit output.
α, β	= Extruder parameters defined in Eqs 2 and 3, respectively.
γ	= Shear strain.
$\dot{\gamma}$	= Rate of shear (sec^{-1}).
$\dot{\gamma}_0$	= $\dot{\gamma}$ in extruder screw channel.
$\dot{\gamma}_{app}$	= Apparent (before Rabinowitsch correction) value of $\dot{\gamma}$.
z	= Flight clearance.
$\dot{\epsilon}$	= Hencky strain rate (s^{-1}).
η	= Viscosity (Pa.s).
η_0, η', η''	= Newtonian, dynamic, and complex η 's.
η_{app}	= Apparent η .
$\eta_e, \eta_e', \eta_{e,0}$	= Elongational viscosity, its tran-

sient, and limiting value at $\dot{\epsilon} \rightarrow 0$, respectively (Pa.s).

η_2	= η_e' value at the onset of steady state deformation (see Ref. 14).
ρ	= Density (kg/L).
σ_{12}	= Shear stress (Pa).
$\sigma_{11} - \sigma_{22} = N_1$	= First normal stress difference (Pa).
σ_{11}	= Uniaxial elongational stress.
σ_p	= Slit-die entrance correction factor.
ϕ	= Screw helix angle.
ω	= Frequency (radians/s).
ω_x	= ω -value at which $G' = G'' = G_x$.

DISCUSSION: L. A. UTRACKI AND A. M. CATANI

M. E. Ryan: This is an interesting paper. You presented a good set of data and the demonstration of the agreement between flow curves as determined in a viscometer and computed from the slit-die is quite gratifying. What escapes me is the reason for which these studies were undertaken. What was the guiding idea and what is the main conclusion?

L. A. Utracki: I feel increasingly unhappy about the gap between the rheology and mathematical modeling of plastics flow, about the difference between what rheologists measure and discuss and what the modeling engineers use. Here you have a very simple experiment; four PE resins (i.e. in the melt the thermodynamic parameters are nearly the same) with well determined rheological parameters for the shear, oscillatory, and elongational flows. We decided to measure the relative behavior of these resins in a single screw extruder only in the metering and die zones. In principle, knowing the rheology we should be able to predict the behavior quite well. Well, we did not. For flow in the metering zone we used the usual assumptions that: each stage of the extrusion process can be analyzed separately, and in the metering zone only the shear flow is important. It is obvious that these assumptions are not valid. For the die flow there are two important observations: for higher molecular weight LDPE's shear disentanglement is important (and it cannot be predicted from a capillary flow), and for short dies (e.g. as the rod die) the $1/d$ correction depends on the nature of the polymer, i.e. the "universal correction" used by designers of extrusion dies is a simplification. The results indicate that the primary reason for these failures is neglect of the elongational viscosity.

J. Vlachopoulos: In modeling the convergent flow through a slit die we had to introduce both the first normal stress difference and the elongational viscosity. The latter function was particularly important for flow at high Deborah number.

L. A. Utracki: Yes, this is my point. In modeling the extruder performance one has to use a complete description of the material. In the recent film in

flows of non-Newtonian liquids, Prof. K. Walters dramatically illustrated this point using two liquids of the same zero shear viscosity flowing through tubes with and without a convergence. In the absence of convergence the Newtonian liquid flowed more slowly than the shear thinning non-Newtonian one. In the presence of convergence the reverse was true—the elongational viscosity over-compensated the shear thinning effect.

K. Koyama: You showed the dependence: $\log \eta'_e$ versus $\log t$ for all three types of PE. For each the form was quite different. Do you think that this is typical? Can one characterize the type of PE using this plot.

L. A. Utracki: Only to a certain extent. The dependence gives information on all three basic molecular parameters: molecular weight—by the level of η'_e at large t proportional to η_0 , molecular weight distribution—by the slope of the dependence at the intermediate times, and branching—by the magnitude of the strain hardening branches. Since the LLDPE sample had low molecular weight and a narrow molecular weight distribution the slope was low and there was no evidence of strain hardening. Recently we measured η'_e of a high molecular weight LLDPE with a broad distribution. Here the slope was found to be relatively steep and the strain hardening was quite apparent.

An Engineering Study of the Film Embossing Process

M. R. KAMAL, A. HABER

*Department of Chemical Engineering
McGill University
Montreal, Canada H3A 2A7*

and

M. E. RYAN

*Department of Chemical Engineering
State University of New York at Buffalo
Amherst, New York 14260*

A mathematical model of the dynamics and heat transfer of the film embossing process has been developed. The thermal analysis around the preheat roll is determined from an unsteady, two-dimensional heat conduction equation along with appropriate boundary conditions by neglecting the curvature of the preheat roll and choosing a Lagrangian reference frame. The heat transfer occurring between the preheat roll and the embossing rolls is based on a one-dimensional analysis, including both convective and radiative effects. The deformation occurring in the nip region is analyzed for two different situations. For the case where the surface features are small in comparison with the film thickness, a modified one-dimensional calendering analysis is given, accounting for the irregular geometry of the embossing roll surface. For the case where the polymer does not make complete contact with the surface of the engraved channel, the local deformation is determined by means of a simple one-dimensional cavity filling model. The required pressure distribution is determined by means of a simple one-dimensional cavity filling model. The required pressure distribution is determined by means of a conventional calendering analysis. The analysis for the case of a Newtonian and power-law model is presented in detail. The model yields qualitatively correct results and is computationally simple.

INTRODUCTION

The embossing of thermoplastic films has become commercially significant in recent years due to the increasing demand for imparting a design, pattern, or texture for a particular product application. Current large scale applications include disposable articles such as hospital pads, diapers, bags, and package overwraps. Embossed plastic film will continue to successfully penetrate commercial markets previously dominated by paper or metal foil.

The embossing of a thermoplastic surface is generally accomplished by having the polymer available in a softened plastic state and conferring the desired pattern by forcing the material through the nip of two embossing rolls. At least one of the embossing rolls possesses an engraved design in order to impart the desired pattern. Frequently the embossing rolls are cooled so as to accurately fix the embossed design. The embossments may be

intended to satisfy a variety of different objectives. These include the enhancement of the aesthetic quality of a consumer product, the improvement of ultimate properties, or the elimination of poor surface quality or imperfections yielding a film with acceptable finish. The process may be carried out directly on-line in conjunction with a slot cast or blown film extrusion process, or it may be run as a separate autonomous operation.

A wide range of different embossing operations, embossing roll configurations, and heating systems are found in industrial practice. A typical film embossing line is depicted schematically in Fig. 1. A thin thermoplastic film is produced in a conventional tubular blown film extrusion process. The thermomechanical history experienced by the polymer during the film blowing step imparts a particular orientation and microstructure to the film. The film then passes over a preheat roll and through a

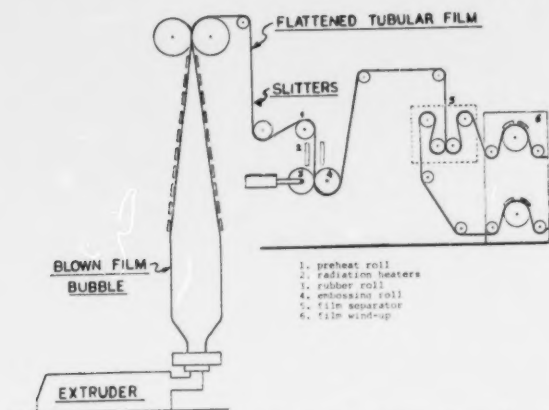


Fig. 1. Schematic diagram of the tubular blown film embossing process.

series of radiation heaters. The thermal treatment results in stress relaxation and possible morphological changes. The film is then fed to the nip of the embossing rolls, which imprints the desired surface pattern. Lower embossing roll temperatures generally correspond to better reproduction of the engraved design.

Apart from the extensive literature directly related to slot cast extrusion, blown film extrusion, and calendaring, to the best of our knowledge no quantitative analysis of plastics embossing operations has been published to date. An understanding of the dynamics and heat transfer of the embossing process is necessary for ascertaining the effect of the thermal and stress history on the physical dimensions, orientation, morphology, and ultimate properties of the final embossed product. The emphasis of this paper is therefore concerned with the development of engineering techniques for the experimental and mathematical treatment of the heat transfer and stress history associated with the embossing operation in order to be able to predict the final physical dimensions and characteristics of the embossed film.

EXPERIMENTAL

The experimental results reported in this paper were obtained on a tubular blown film embossing line, as shown in Fig. 1. The embossing section of the process consisted of a water-heated preheat roll, two 4-tube radiation heater units placed on either side of the free moving film, and a water-cooled embossing/rubber roll system, as depicted in Fig. 2. The tubular film was produced on a Black-Clawson film line using either a 5 or 10 inch annular die. Two commercial polyethylene film resins were used in this study, namely, a Union Carbide low-density polyethylene (4409) and a Union Carbide linear low-density polyethylene (7047). Characterization of the orientation and microstructure of these blown films has been previously reported (1). All film samples had a thickness of 1 to 2 mils and a blow ratio of 3 to 3.5. Temperature measurements were made using a thermocouple surface probe

(Omega Engineering, Model 68203, 68221) and a micro-optical pyrometer (Pyro, Model M-6533).

HEAT TRANSFER ANALYSIS

Prior to embossing, the polymer film undergoes heat treatment by passing over a preheat roll and between two radiation heater tube banks. The purpose of the heat treatment step is to compensate for the thermal losses from the film and to elevate the film temperature close to the melting temperature of the material prior to being fed to the embossing rolls. Too high a temperature can lead to the risk of tearing or damaging the film. The film temperature distribution at the embossing roll nip can have a marked effect on the dimensions and final properties of the embossed film, as is evident in Fig. 3.

Preheat Roll

The preheat roll consists of a water-heated roll 42 inches wide and 11 3/4 inches in diameter. This preheat roll is used to raise the temperature of the polymer film to the range of 93 to 96°C. The polymer film is therefore heated by conduction through contact with the roll surface and loses heat through convective and radiative losses. Since the film thickness is very much smaller than the preheat roll diameter, the curvature of the cylindrical surface may be neglected and the problem may be regarded as two-dimensional unsteady heat conduction in a flat rectangular plate, as shown in Fig. 4.

The following assumptions are made: the film is moving with constant velocity, V , in the x -direction; radiation heat loss is neglected; and the density, specific heat, and thermal conductivity of the polymer are assumed to be constant. Making use of these assumptions, the mathematical description of the problem may be formulated in either a Lagrangian or Eulerian frame of reference. The Lagrangian formulation yields the temperature of a moving material point in the polymer film as a function of time and is given as follows:

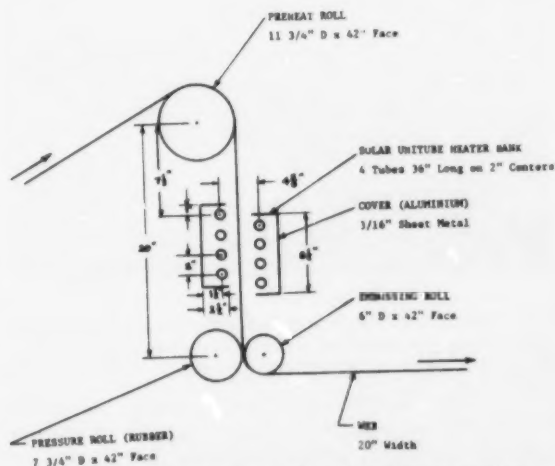
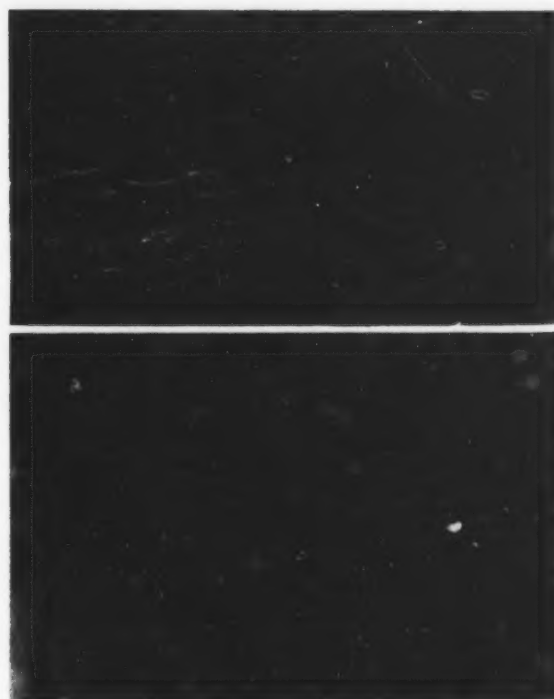
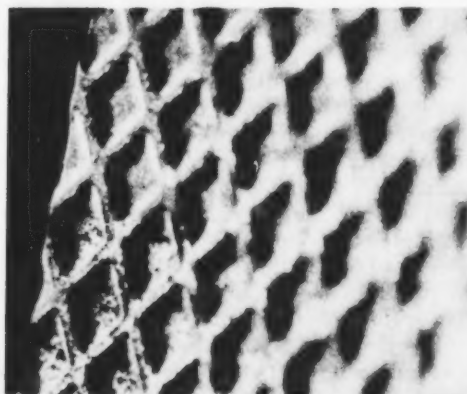


Fig. 2. Schematic diagram of the film embossing section.



(a)



(b)

Fig. 3. Embossed low-density polyethylene film samples. (a) Preheat roll temperature = 93°C, radiation heater temperature = 260°C. (b) Preheat roll temperature = 93.3°C, radiation heater temperature = 815°C.

$$\rho C_p \frac{DT}{Dt} = k \left(\frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \quad (1)$$

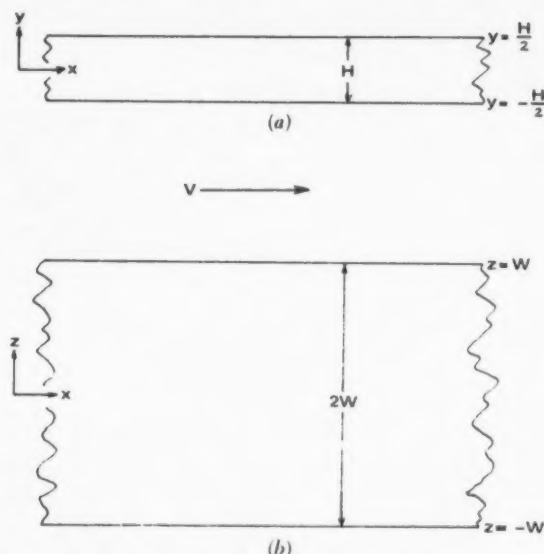


Fig. 4. Schematic diagram of film geometry for heat transfer analysis. (a) Edge view. (b) Top view.

$$\text{At } t = 0, T(y, z, 0) = f(y, z) \quad (2)$$

$$\text{At } z = -w,$$

$$-k \frac{\partial T(y, -w, t)}{\partial z} = h(T(y, -w, t) - T_A) \quad (3)$$

$$\text{At } z = w,$$

$$-k \frac{\partial T(y, w, t)}{\partial z} = h(T(y, w, t) - T_A) \quad (4)$$

$$\text{At } y = H/2, T(H/2, z, t) = g(z, t) \quad (5)$$

$$\text{At } y = H/2,$$

$$-k \frac{\partial T(H, z, t)}{\partial y} = h(T(H/2, z, t) - T_A) \quad (6)$$

The initial condition implies that the temperature distribution in the polymer film at the point of contact with the preheat roll is known. The convective heat flux conditions at each edge of the film, given by Eqs 3 and 4, are necessary since the temperature varies across the width of the film due to the fact that the heating water enters on one side of the preheat roll and exits at the other side. Figure 5 gives the experimentally measured temperature variation of the preheat roll surface and outer film surface across the width of the preheat roll. The temperature decreases by approximately 2°C from the water inlet side to the water exit side of the preheat roll. The variability of the experimental data for the film surface temperature results from the inherent experimental difficulties associated with recording the temperature of the rapidly moving film. T_A denotes the ambient air temperature and h is a convective heat transfer coefficient. Equation 5 indicates that the temperature of the polymer film at the point of contact with the steel roll surface is known. The solution of Eqs 1 to 6 gives the temperature of a given material point as a function of time as it passes over the preheat roll. Alterna-

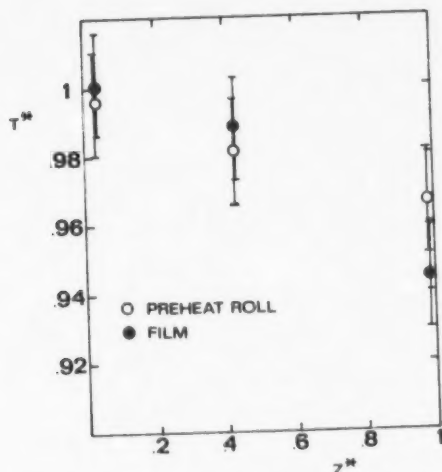


Fig. 5. Temperature variation across the width of the preheat roll at the point of separation of the film from the preheat roll surface.

tively, the Eulerian formulation provides the steady temperature for any spatial position. The two temperature fields are clearly related by virtue of the fact that the x -position of a material point is related to the constant film velocity as follows:

$$x = Vt \quad (7)$$

If the temperature of the heating water remains constant across the width of the preheat roll, edge effects can be neglected and the heat transfer analysis reduces to the simpler one-dimensional formulation. The details of solution for the one-dimensional problem can be found in many standard texts (2).

The solution of the two-dimensional problem was obtained for the Lagrangian formulation, Eqs. 1 to 6, using an implicit finite-difference, alternating-direction, numerical method (3). A value of $0.00048 \text{ cal/cm}^2\text{-s-}^\circ\text{C}$ was chosen for the heat transfer coefficient. This value is consistent with data reported in the literature (4 to 6). Figure 6 shows the variation of the outer film surface temperature as a function of the contact time with the preheat roll, or alternatively, as a function of the position around the preheat roll from the point of contact. For a film velocity of 21 cm/s and a roll diameter of $11\frac{3}{4} \text{ inches}$ (29.85 cm) the total contact time for the polymer is 2.23 s . It is evident from Fig. 6 that the polymer is rapidly heated within a considerably shorter time interval than the total contact time. This implies that the preheating could readily be accomplished using a smaller preheat roll. This would result in reduced capital costs and operating expenses. The calculated temperature distribution across the film thickness is shown in Fig. 7. By the time the polymer separates from the preheat roll the temperature difference across the film thickness is of the order of 0.3°C . Figure 8 gives a comparison of the theoretically calculated temperature variation across the width of the preheat roll at the point of separation with experimentally measured data. The temperature data shown in Fig. 5 were used

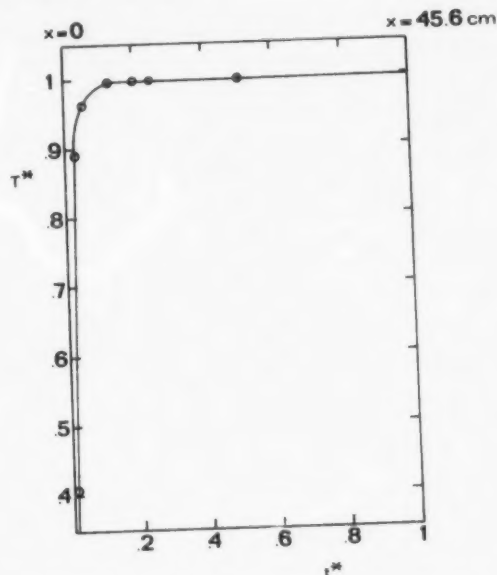


Fig. 6. Variation of outer film surface temperature as a function of contact time.

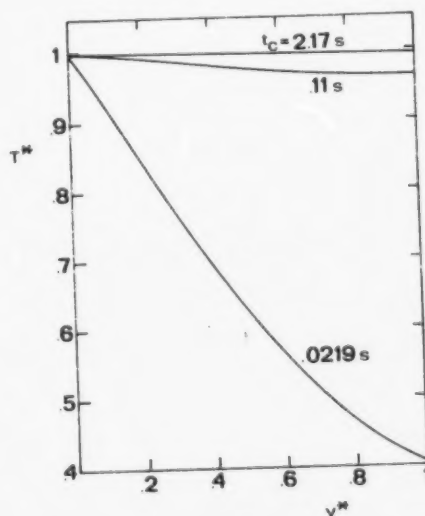


Fig. 7. Calculated temperature distribution across film thickness at various positions around the preheat roll.

for the boundary condition given by Eq 5. The agreement is considered to be reasonable, considering the difficulties associated with the experimental measurements.

Radiation Heaters

After leaving the preheat roll, the polymer film travels 19 cm to the radiation heaters. The two radiation heaters each consist of four horizontal tube radiation heating elements having a length of 36 inches . The tubes are vertically spaced 2 inches from each other and $2\frac{5}{16} \text{ inches}$ from the surface of the travelling film and are staggered with respect to one another on either side of the film. Although the radiation heaters are located some distance

from the preheat roll, the polymer film can be assumed to immediately enter the radiation zone since the total exposure region extends to the vicinity of the preheat roll as shown in Fig. 9.

The high surface temperatures of the radiation heaters give rise to complex natural convection flow patterns around the heating tube bank. Interactions with the boundary layer along the rapidly moving film surface can significantly influence the heat transfer characteristics, and consequently the temperature distribution, in the film. Figures 10 and 11 show typical air temperature distributions measured in the region between the preheat roll and the radiation heaters. Since the transmissivity of air is approximately unity, the high air temperatures are clearly a result of convective effects.

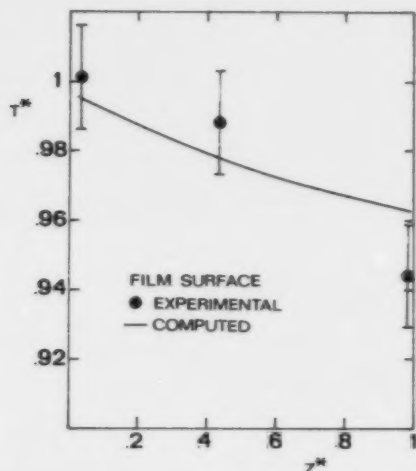


Fig. 8. Temperature variation across the width of the preheat roll at the point of separation.

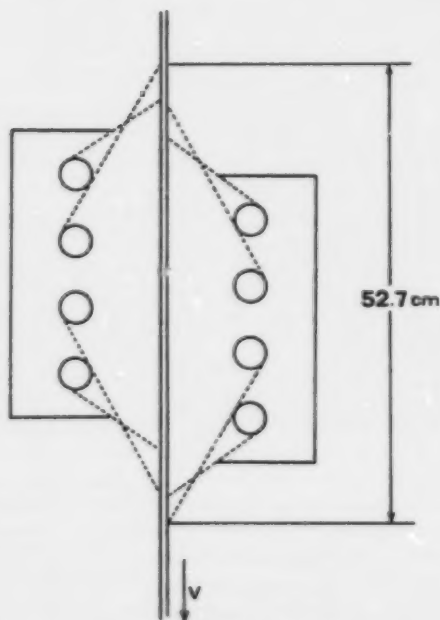


Fig. 9. Radiation zone.

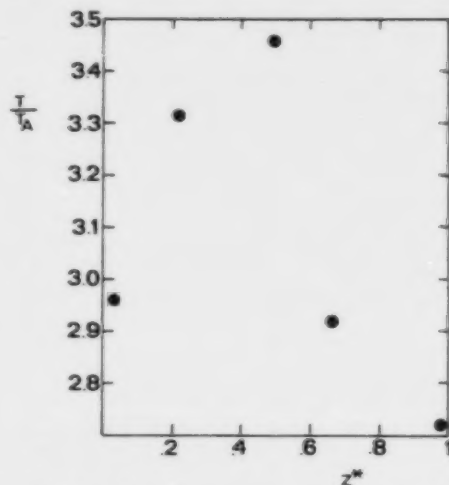


Fig. 10. Variation of air temperature across the width of the film at a position midway between the preheat roll and the radiation heater.

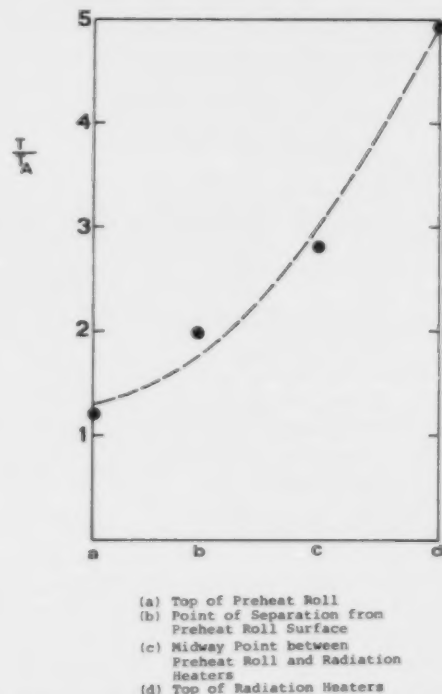


Fig. 11. Variation of air temperature along the film centerline between the preheat roll and the radiation heater.

As a first approximation, a one-dimensional heat transfer analysis has been employed. Temperature variations across the width of the film can be accommodated by applying the one-dimensional analysis to individual segments across the film. The relevant governing equation and boundary conditions for the Lagrangian formulation are given as follows:

$$\rho C_p \frac{DT}{Dt} = k \frac{\partial^2 T}{\partial y^2} \quad (8)$$

$$\text{At } t = 0, T(y, 0) = f_1(y) \quad (9)$$

$$\text{At } y = 0, \frac{\partial T\left(\frac{H}{2}, t\right)}{\partial y} = 0 \quad (10)$$

$$\begin{aligned} \text{At } y = H/2, -k \frac{\partial T(H/2, t)}{\partial y} \\ = -\epsilon(2 - \epsilon)F\sigma(T_R^4 - T(H/2, t)^4) \quad (11) \\ + h(T(H/2, t) - T_A) \end{aligned}$$

The Eulerian formulation could equivalently be used. Although the radiation tubes on each side of the film are staggered with respect to one another, Eq 10 assumes that the temperature profile across the film is symmetric. The first term on the right-hand side of Eq 11 represents the radiant energy absorbed by the polymer film where ϵ is the emissivity of the polymer, F is the shape factor, σ is the Stefan-Boltzmann constant, and T_R is the radiation heater temperature. An emissivity value of 0.15 was used and is consistent with the value estimated from the infrared spectrum of polyethylene (5). The shape factor is calculated by considering a small rectangular element on the surface of the traveling film. The shape factor distribution along the film is a function of the size of the rectangular element chosen, and the geometry of the heater system and is shown in Fig. 12. The details of the calculation can be found elsewhere (7). The single remaining difficulty resides in the specification of the ambient air temperature, T_A . As mentioned previously, a rigorous analysis of the convective air motion poses a formidable problem. For the purposes of a preliminary analysis, an ambient air temperature distribution has been assumed based on the experimental data given in Figs. 10 and 11. This assumed air temperature distribution is shown in Fig. 13. It should be kept in mind that the experimental data shown in Figs. 10 and 11 are typical representative values that vary considerably with spatial position. Also, these data were obtained either above or

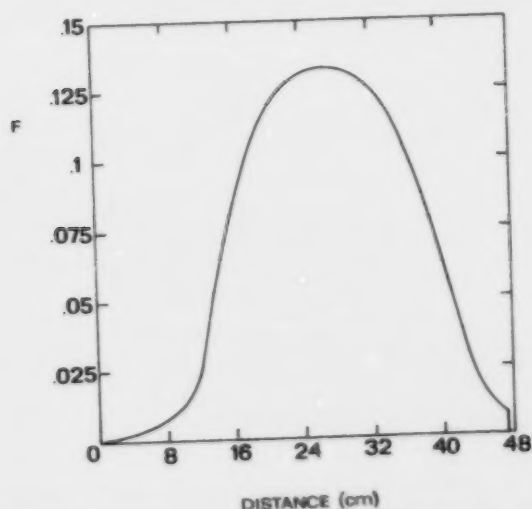


Fig. 12. Shape factor distribution within the radiation zone.

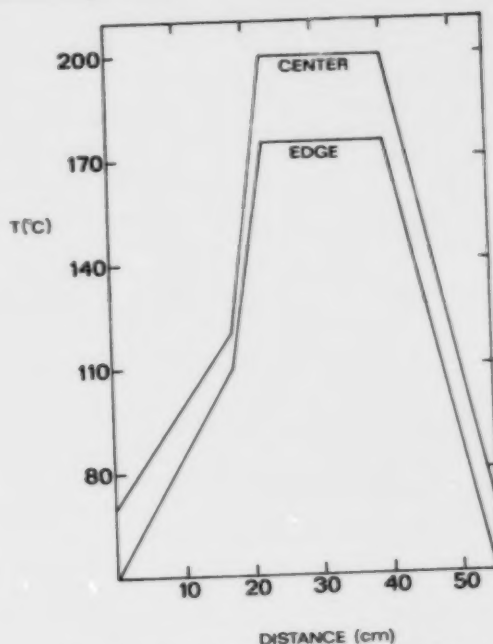


Fig. 13. Assumed air temperature distribution.

below the radiation heaters. It is extremely difficult to measure temperature distributions around the tubular radiation heaters due to the limited space and high temperatures involved. In addition, extreme caution must be exercised in order to eliminate radiant energy absorption by the temperature sensor. Currently, efforts are being made to develop better predictive methods and more complete experimental data regarding the ambient air temperature distribution.

Figure 14 shows the variation of film surface temperature as a function of travel distance from the preheat roll. Initially the polymer film cools slightly, but then rapidly increases in temperature. The separate effects due to convection and radiation are also shown in the figure. It is evident that convection is a controlling factor in determining the final temperature profile. A comparison between the theoretically calculated temperature distribution across the film width with experimentally measured film surface temperatures is shown in Fig. 15. The agreement is considered to be reasonable as a first approximation in view of the uncertainties associated with the experimental measurements and the assumptions underlying the theoretical calculations.

STRESS FIELD ANALYSIS

The film blowing process gives rise to an oriented crystalline polymer film. The thermal history experienced by the polymer film in passing over the preheat roll and through the radiation zone could give rise to the development of retractive stresses due to the elevation in temperature of the oriented film. In order to ascertain if the development of such stresses could be significant, film samples were annealed for 10, 30, 60, and 300 seconds at tem-

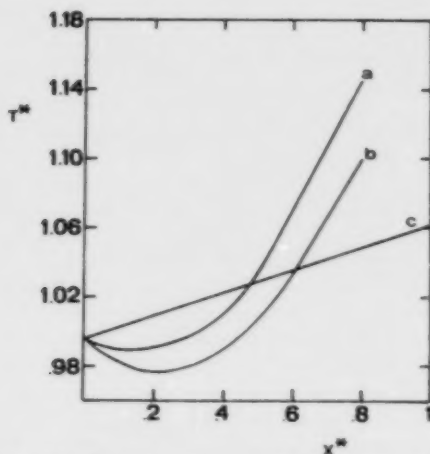


Fig. 14. Film surface temperature as a function of travel distance. (a) Combined convection and radiation. (b) Convection only. (c) Radiation only.

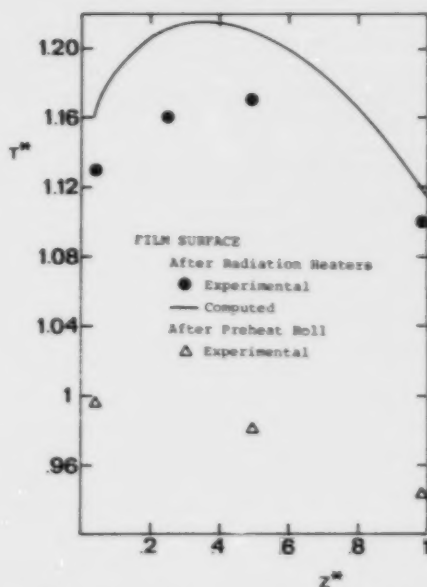


Fig. 15. Surface temperature variation across the width of the polymer film.

peratures of 55, 75, and 100°C in a forced convection oven, and shrinkage in the machine direction was measured. The results are shown in Fig. 16. The data indicate that very little shrinkage occurs over short time periods or at low annealing temperatures. Under normal operating conditions the maximum travel time for the polymer to reach the embossing rolls is of the order of 3 seconds or less. Therefore, it is reasonable to conclude that no significant thermal stresses are developed in the polymer film as a consequence of the brief thermal pretreatment. In addition, no large external stresses are imposed on the material in this region since the film, preheat, and embossing rolls are all normally operated at the same linear velocity. Thus, any significant stresses, deformations, and microstruc-

tural changes are assumed to be confined to the nip region between the two embossing rolls.

In many respects the embossing operation resembles either the cold rolling or the calendering process. However, in the usual calendering analyses (8 to 15) the two calendering rolls are assumed to be smooth cylinders having the same diameter. Analyses involving calender rolls of unequal size or unequal speed have been made using either bipolar coordinates (16 to 18) or a finite element numerical method (19). In the film embossing process, the size of the two embossing rolls may differ and at least one of the embossing rolls does not possess a smooth cylindrical surface.

A schematic cross-sectional view of two different embossing situations is depicted in Fig. 17. Figure 17a illustrates a situation where the surface features or variations along the embossing roll surface are small in comparison to the film thickness. The polymer is assumed to be in complete contact with the embossing roll surface throughout the nip region. These conditions are particularly relevant for matte finish embossing processes. The case where deep grooves or a deeply engraved pattern exists on the embossing rolls is shown in Fig. 17b and typifies

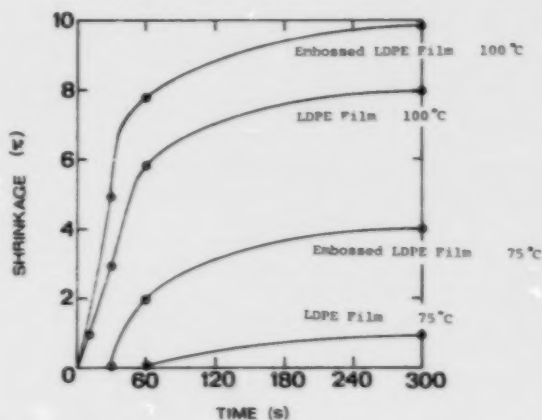


Fig. 16. Shrinkage as a function of time for unembossed and embossed low-density polyethylene film samples.

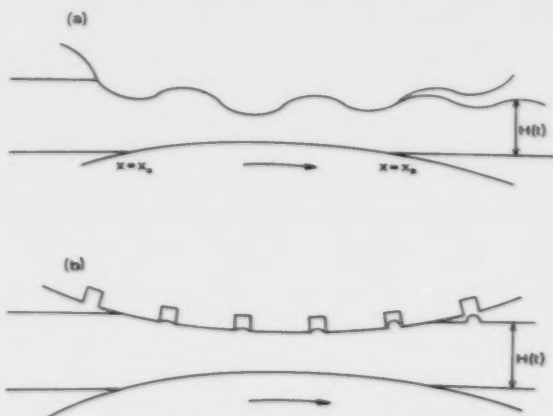


Fig. 17. Cross-sectional view of embossing rolls. (a) Complete contact with embossing roll surface. (b) Incomplete contact with embossing roll surface.

many pattern or design embossing operations. This situation results in incomplete contact of the polymer with the roll surface. Therefore, from the point of view of the local dynamics of the process in the vicinity of a region of incomplete contact, the deformation is more closely analogous to that encountered in thermoforming or mold filling.

Complete Contact Analysis

Figure 18 schematically depicts the cross-sectional view of two embossing rolls in complete contact with the polymer in the nip region. The figure also serves to define the relevant geometrical parameters. The radii of the embossing rolls are denoted as R_1 and R_2 , respectively, and the distance between centers is denoted as L . The definition of the roll surface is given by specifying the radial distance to the surface as a function of the angular position relative to some reference. Therefore

$$R_{S1}(\theta) = R_1 + \epsilon_1(\theta) \quad (12)$$

$$R_{S2}(\theta) = R_2 + \epsilon_2(\theta) \quad (13)$$

When the rolls are rotating, the surface features continually change position and the roll surface can be defined with respect to stationary coordinates as follows:

$$R_{S1}(\theta, t) = R_1 + \epsilon_1(\theta - \omega_1 t) \quad (14)$$

$$R_{S2}(\theta, t) = R_2 + \epsilon_2(\theta - \omega_2 t) \quad (15)$$

ω_1 and ω_2 denote the angular velocities of the two embossing rolls, respectively. These embossing roll surfaces can alternatively be defined by the functions $h_1(x, t)$ and $h_2(x, t)$, respectively, as indicated in Fig. 19. Thus

$$h_1(x, t) = h_1(o, t) + R_{S1}(o, t) - (R_{S1}^2(\theta, t) - x^2)^{1/2} \quad (16)$$

$$h_2(x, t) = h_2(o, t) + R_{S2}(o, t) - (R_{S2}^2(\theta, t) - x^2)^{1/2} \quad (17)$$

It is important to keep in mind that the functions

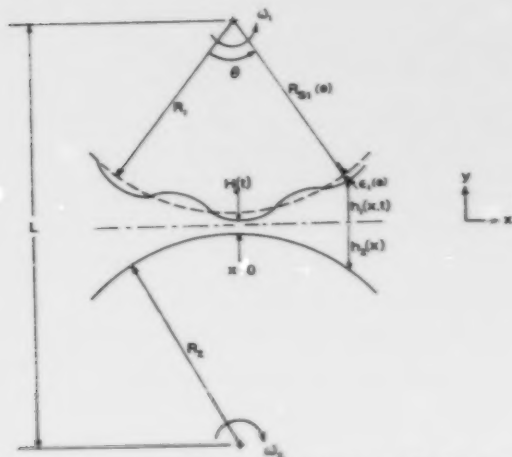


Fig. 18. Cross-sectional view of embossing rolls for complete contact analysis.

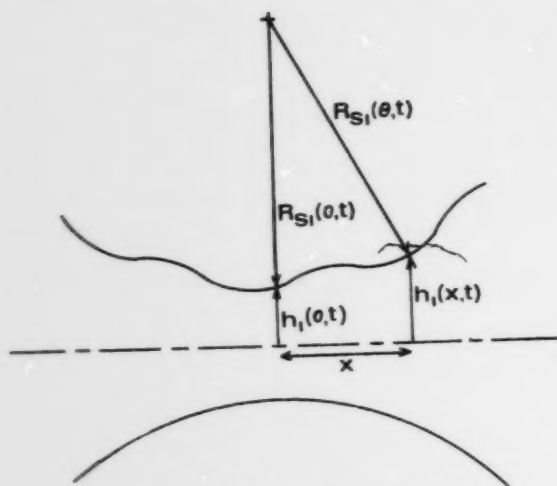


Fig. 19. Definition of embossing roll surfaces.

R_{S1} and R_{S2} given by Eqs 14 and 15, or h_1 and h_2 given by Eqs 16 and 17, can be completely determined from a knowledge of the geometry and rotational speeds of the embossing rolls. It should be readily apparent that the gap or distance between the embossing roll surfaces will also depend on time.

$$H_o(t) = h_1(o, t) + h_2(o, t) \quad (18)$$

$$= L - R_{S1}(o, t) - R_{S2}(o, t)$$

The embossed film thickness will likewise be a time dependent function and is denoted as $H(t)$.

Since the polymer undergoes permanent deformation in the embossing operation it is considered to be in a molten state during the process. The deformation of the polymer film in a solidified state can be described by means of a cold forming analysis, but the details will not be considered here. Commercially the melt embossing process has the attraction of higher operating speeds or throughput rates. From a careful consideration of the physics of the process the following assumptions are considered to be justified: the flow is assumed to be laminar; the fluid is considered to be incompressible; the flow is assumed to be strictly two dimensional—all variations across the width of the embossing rolls are neglected; and all body forces are negligible.

Generally, the film thickness and the gap in the nip region are very much smaller than the embossing rolls. Under these conditions the lubrication approximation can be applied and the flow can reasonably be assumed to be one dimensional ($V_y \ll V_x$, $\frac{\partial}{\partial x} \ll \frac{\partial}{\partial y}$). Inertial effects may be considered negligible due to the highly viscous nature of the polymer melt. Thermal conduction in the x -direction is also neglected. Invoking the above assumptions results in the following simplification of the rate of deformation tensor and the governing equations of change:

$$\underline{\underline{A}} = \begin{bmatrix} 2 \frac{\partial V_x}{\partial x} & \frac{\partial V_x}{\partial y} & 0 \\ \frac{\partial V_x}{\partial y} & 2 \frac{\partial V_y}{\partial y} & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (19)$$

$$\frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} = 0 \quad (20)$$

$$\rho \frac{\partial V_x}{\partial t} = -\frac{\partial P}{\partial x} + \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} \quad (21)$$

$$\rho C_v \left(\frac{\partial T}{\partial t} + V_x \frac{\partial T}{\partial x} \right) = \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) + \tau_{xy} \frac{\partial V_x}{\partial y} \quad (22)$$

In addition to Eqs 19 to 22, a constitutive equation is required in order to relate the stress field to the rate of deformation. The constitutive equation generally contains a temperature dependent material function, which thereby couples Eqs 21 and 22. The governing equations, along with the appropriate boundary and initial conditions, would therefore require some sort of numerical scheme for solution. The ordinary calendaring problem has been successfully analyzed in this manner using a finite element method (20, 21).

Newtonian Model

The constitutive equation for a Newtonian fluid may be expressed as follows

$$\underline{\underline{\tau}} = \mu \underline{\underline{A}} \quad (23)$$

It is further assumed that the flow is quasi-steady state and isothermal. The quasi-steady state assumption implies that the contribution due to the time derivative in Eq 21 is negligible in comparison to the other terms. However, it should be noted that the velocity and pressure distributions will be functions of time since the boundary conditions are time dependent. As a result of the above considerations, Eq 21 becomes

$$\frac{\partial P}{\partial x} = \mu \frac{\partial^2 V_x}{\partial y^2} \quad (24)$$

subject to the boundary conditions

$$\text{At } y = -h_1(x, t), \quad V_x = V_1(x, t) \quad (25)$$

$$\text{At } y = h_2(x, t), \quad V_x = V_2(x, t) \quad (26)$$

The velocities V_1 and V_2 are readily determined from the geometry and rotational speeds of the embossing rolls. Integration of Eq 24 yields

$$V_x = \frac{1}{2\mu} \left(\frac{\partial P}{\partial x} \right) y^2 + C_1 y + C_2 \quad (27)$$

Applying Eqs 25 and 26 to Eq 27 gives

$$C_1 = \frac{V_2 - V_1}{h_2 + h_1} - \frac{1}{2\mu} \left(\frac{\partial P}{\partial x} \right) (h_2 - h_1) \quad (28)$$

$$C_2 = \frac{V_1 + V_2}{2} - \frac{1}{2} \frac{(V_2 - V_1)(h_2 - h_1)}{(h_2 + h_1)} - \frac{1}{2\mu} \left(\frac{\partial P}{\partial x} \right) h_1 h_2 \quad (29)$$

For the ordinary calendaring situation, $V_1(x, t) = V_2(x, t) = V$, $h_1(x, t) = h_2(x, t) = h(x)$, and Eqs 27, 28, and 29 reduce correctly to the following

$$C_1 = 0 \quad (30)$$

$$C_2 = V - \frac{1}{2\mu} \left(\frac{dP}{dx} \right) h^2 \quad (31)$$

$$V_x = V + \frac{1}{2\mu} \left(\frac{dP}{dx} \right) (y^2 - h^2(x)) \quad (32)$$

The volumetric flow rate is related to the velocity as follows

$$Q = W \int_{y=-h_1(x,t)}^{y=h_2(x,t)} V_x dy \quad (33)$$

where W denotes the width of the embossed film and any arbitrary axial position may be chosen for evaluation of the integral. Substituting Eqs 27 to 29 into Eq 33 and integrating gives

$$Q = W \left[-\frac{1}{4\mu} \left(\frac{\partial P}{\partial x} \right) \left(\frac{1}{3}(h_1^3 + h_2^3) + h_1^2 h_2 + h_1 h_2^2 \right) + \frac{(V_1 + V_2)(h_1 + h_2)}{2} \right] \quad (34)$$

For the ordinary calendaring case, Eq 34 properly reduces to

$$Q = W \left[2Vh - \frac{2h^3}{3\mu} \left(\frac{dP}{dx} \right) \right] \quad (35)$$

Solving Eq 34 for the pressure gradient yields

$$\begin{aligned} \frac{\partial P}{\partial x} &= \frac{6\mu(V_1 + V_2)(h_1 + h_2) - 12\mu Q/W}{(h_1 + h_2)^3} \\ &= \frac{6\mu(V_1 + V_2)}{(h_1 + h_2)^2} - \frac{12\mu Q}{W(h_1 + h_2)^3} \end{aligned} \quad (36)$$

At some upstream location $x = x_0$, the pressure has some known or specified value $P = P_0$. Equation 36 may therefore be integrated to yield the pressure distribution. At some downstream location the film will detach from the embossing rolls. This detachment point is designated as $x = x_D$ and the pressure is atmospheric, $P = P_A$. Therefore the point of detachment can be calculated from the pressure distribution. Also, at the point of detachment the velocity profile is flat and therefore $\frac{\partial V_x}{\partial y} = \frac{\partial^2 V_x}{\partial y^2} = 0$. From Eqs. 24 and 36 this implies

$$W[V_1(x_D, t) + V_2(x_D, t)][h_1(x_D, t) + h_2(x_D, t)] - 2Q = 0 \quad (37)$$

Equation 37 is a simple material balance relating the volumetric flow rate to the take-up speed and final film thickness. For the ordinary calendering case Eq 37 becomes

$$Q = VWH \quad (38)$$

It should be noted that the pressure distribution and the detachment point can vary significantly with time due to the time dependency of the boundary conditions. Figure 20 shows the point of attachment as a function of the point of detachment as commonly given in conventional calendering analyses. From a computational point of view, it is generally easier to specify the detachment point, determine the corresponding volumetric flow rate, and integrate Eq 36 in the upstream direction in order to ascertain the pressure distribution and the point of attachment. Figure 20 indicates that for the ordinary calendering operation there exists a unique, well-defined relationship between the attachment and detachment points. However, for the embossing situation this relation varies with time due to the changing geometry in the nip region. This variation is shown in Fig. 20 for the case of an embossing roll having a surface defined by a sinusoidal function. Figure 21 shows the time variation of attachment point location for a prescribed location of the detachment point. As is evident in the figure, the magnitude of the variability is directly related to the surface variation (in this case, the amplitude of the sinusoidal function). The pressure distribution in the nip is extremely sensitive to changes in either the point of attachment or detachment, as can be seen in Fig. 22. This has been long recognized from conventional calendering analyses (22). Since these contact locations continuously change during the embossing process, the

pressure distribution can vary dramatically, as shown in Fig. 22. Figure 23 shows the time variation of pressure at a fixed location for the case of the sinusoidal embossing roll surface. It should be kept in mind that the upstream attachment point, x_p , can be directly related to the thickness of the film being fed to the embossing rolls and that the final thickness of the embossed film could then be calculated as a function of time and compared with experimental data.

The force tending to separate the embossing rolls may be determined by integration of the pressure

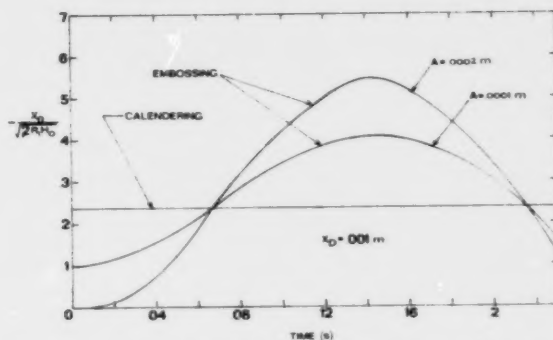


Fig. 21. Variation of attachment point location as a function of time for a specified detachment point position.

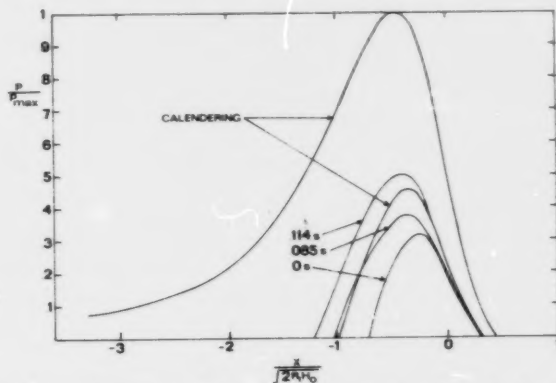


Fig. 22. Pressure distribution in the nip region for calendering and embossing situations.

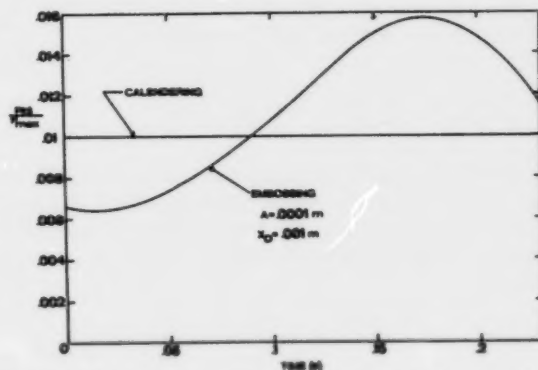


Fig. 23. Variation of pressure as a function of time for a specified location in the nip region.

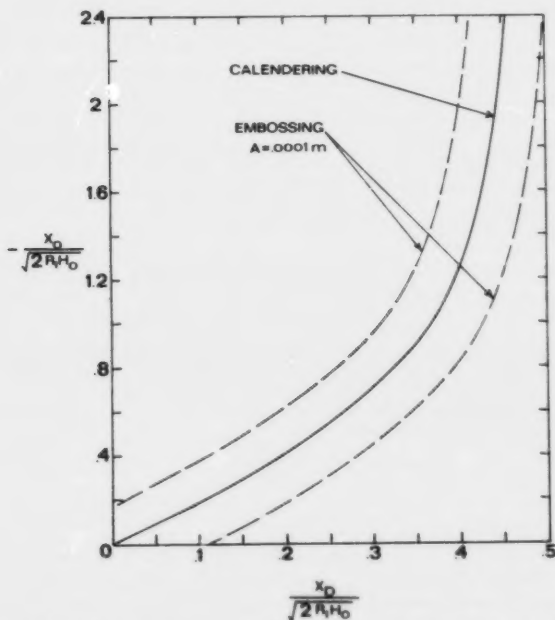


Fig. 20. Relationship between point of attachment and point of detachment for calendering and embossing situations.

distribution. Thus

$$\frac{F}{W} = \int_{x=x_0}^{x=x_D} P(x, t) dx \quad (39)$$

Since the force on the embossing rolls is either preset or measured, Eq 39 provides another means for testing the mathematical model. The adiabatic temperature rise in the fluid is given by

$$\Delta T = \frac{\dot{W}}{\rho Q C_p} \quad (40)$$

where $\dot{W}$ denotes the power input to the fluid by the embossing rolls and may be calculated as follows

$$\begin{aligned} \dot{W} &= W \int_{x=x_0}^{x=x_D} \tau_{yx}|_{y=-h_1(x,t)} V_1(x, t) dx \\ &+ W \int_{x=x_0}^{x=x_D} \tau_{yx}|_{y=h_2(x,t)} V_2(x, t) dx \\ &= W \int_{x=x_0}^{x=x_D} \left[\frac{\mu(V_2 - V_1)}{h_2 + h_1} - \frac{\partial P}{\partial x} \left(\frac{h_2 + h_1}{2} \right) \right] V_1 dx \\ &+ W \int_{x=x_0}^{x=x_D} \left[\frac{\mu(V_2 - V_1)}{h_2 + h_1} + \frac{\partial P}{\partial x} \left(\frac{h_2 + h_1}{2} \right) \right] V_2 dx \end{aligned} \quad (41)$$

Substituting Eq 36 into Eq 41 gives

$$\begin{aligned} \dot{W} &= W \int_{x=x_0}^{x=x_D} \left[\frac{6\mu Q}{W(h_1 + h_2)^2} - \frac{2\mu(2V_1 + V_2)}{h_1 + h_2} \right] V_1 dx \\ &+ W \int_{x=x_0}^{x=x_D} \left[\frac{2\mu(V_1 + 2V_2)}{h_1 + h_2} - \frac{6\mu Q}{W(h_1 + h_2)^2} \right] V_2 dx \end{aligned} \quad (42)$$

Power-Law Model

For the case of a power-law fluid, the following constitutive equation may be written

$$\underline{\underline{\tau}} = K \left(\frac{\underline{\underline{II}}_\Delta}{2} \right)^{\frac{n-1}{2}} \underline{\underline{\dot{\epsilon}}} \quad (43)$$

where $\underline{\underline{II}}_\Delta$ denotes the second scalar invariant of the rate of deformation tensor. Making use of the same basic assumptions as in the previous Newtonian analysis implies that the shear stress is given as follows

$$\tau_{yx} = K \left| \frac{\partial V_x}{\partial y} \right|^{n-1} \frac{\partial V_x}{\partial y} \quad (44)$$

Invoking the same assumptions as in the previous

analysis enables the equation of motion to be expressed as

$$\frac{\partial P}{\partial x} = \frac{\partial}{\partial y} \left(K \left| \frac{\partial V_x}{\partial y} \right|^{n-1} \frac{\partial V_x}{\partial y} \right) \quad (45)$$

Integrating Eq 45 with respect to y yields

$$\frac{\partial V_x}{\partial y} = \left(\frac{\partial P}{\partial x} \frac{y}{K} + \frac{C_1}{K} \right)^{1/n} \quad (46)$$

Integrating Eq 46 with respect to y finally gives

$$V_x = \frac{\frac{nK}{n+1} \left(\frac{\partial P}{\partial x} \frac{y}{K} + \frac{C_1}{K} \right)^{\frac{n+1}{n}}}{\frac{\partial P}{\partial x}} + C_2 \quad (47)$$

Applying the boundary conditions given by Eqs 25 and 26 results in the following two relationships

$$V_1 = \frac{\frac{nK}{n+1} \left(\frac{\partial P}{\partial x} \left(\frac{-h_1}{K} \right) + \frac{C_1}{K} \right)^{\frac{n+1}{n}}}{\frac{\partial P}{\partial x}} + C_2 \quad (48)$$

$$V_2 = \frac{\frac{nK}{n+1} \left(\frac{\partial P}{\partial x} \frac{h_2}{K} + \frac{C_1}{K} \right)^{\frac{n+1}{n}}}{\frac{\partial P}{\partial x}} + C_2 \quad (49)$$

Subtracting Eq 49 from Eq 48 gives

$$\begin{aligned} \frac{nK}{n+1} \left[\left(\frac{\partial P}{\partial x} \left(\frac{-h_1}{K} \right) + \frac{C_1}{K} \right)^{\frac{n+1}{n}} - \left(\frac{\partial P}{\partial x} \frac{h_2}{K} + \frac{C_1}{K} \right)^{\frac{n+1}{n}} \right] \\ V_1 - V_2 = \frac{\frac{\partial P}{\partial x}}{\frac{\partial P}{\partial x}} \end{aligned} \quad (50)$$

Substituting Eq 47 into Eq 33 yields the following expression for the volumetric flow rate

$$\begin{aligned} Q = W \frac{\frac{n^2 K^2}{(n+1)(2n+1)} \left[\left(\frac{\partial P}{\partial x} \frac{h_2}{K} + \frac{C_1}{K} \right)^{\frac{2n+1}{n}} - \left(\frac{\partial P}{\partial x} \left(\frac{-h_1}{K} \right) + \frac{C_1}{K} \right)^{\frac{2n+1}{n}} \right]}{\left(\frac{\partial P}{\partial x} \right)^2} \\ + C_2(h_1 + h_2) \end{aligned} \quad (51)$$

For the case of a Newtonian fluid, $n = 1$, and Eqs 50 and 49 can be explicitly solved for C_1 and C_2 , yielding identical expressions to those derived in the previous section. For the general non-Newtonian case, $n \neq 1$, and no simple explicit

expressions for C_1 and C_2 can be obtained. Equations 49 to 51 must be solved simultaneously by an appropriate numerical scheme in order to determine C_1 , C_2 , and the unknown pressure gradient $\frac{\partial P}{\partial x}$ for desired values of x and t . Numerical integration of the data is then required in order to obtain the pressure distribution.

More complicated constitutive equations preclude any simple analytical solution and necessitate direct numerical solution of the relevant governing equations.

Incomplete Contact Analysis

A cross-sectional view of the embossing operation corresponding to incomplete contact is shown in Fig. 24. The analysis of the dynamics in the nip region is considered to be closely approximated by means of a conventional calendering analysis. The general governing equations are given by Eqs 19 to 22. The local deformation in the vicinity of incomplete contact is analyzed separately.

Newtonian Model

The equation of motion for the steady, isothermal calendering of a Newtonian fluid is given as follows

$$\frac{dP}{dx} = \mu \frac{\partial^2 V_x}{\partial y^2} \quad (52)$$

subject to the boundary conditions

$$\text{At } y = 0, \quad \frac{\partial V_x}{\partial y} = 0 \quad (53)$$

$$\text{At } y = h(x), \quad V_x = V \quad (54)$$

The resulting velocity profile, volumetric flow rate, and pressure distribution are therefore given by the following expressions

$$V_x = V + \frac{y^2 - h^2(x)}{2\mu} \left(\frac{dP}{dx} \right) \quad (55)$$

$$Q = W \left[2Vh - \frac{2h^3}{3\mu} \left(\frac{dP}{dx} \right) \right] \quad (56)$$

$$\frac{dP}{dx} = \frac{3\mu V}{h^2} - \frac{3\mu Q}{2h^3 W} \quad (57)$$

From Fig. 19 it is apparent that

$$h = H_o + R - (R^2 - x^2)^{1/2} \quad (58)$$

Equation 58 can be substituted into Eq 57 and the resulting equation integrated in order to yield the pressure distribution. For most practical purposes $x \ll R$ and $h(x)$ may be represented to a good approximation as follows

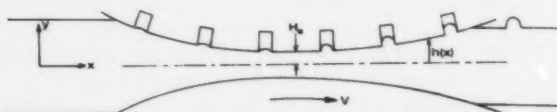


Fig. 24. Cross-sectional view of embossing rolls for incomplete contact analysis.

$$h = H_o \left(1 + \frac{x^2}{2H_o R} \right) \quad (59)$$

Some calendering results are shown in Figs. 20 and 22. More detailed results can be found elsewhere (9, 10, 22, 23).

From a knowledge of the known pressure distribution in the nip region it is now possible to analyze the local deformation that occurs in the vicinity of the engraved channel. The flow of material into the engraved channel is regarded as analogous to the mold filling of an empty channel. As a first approximation the flow will be regarded as a simple quasi-steady state, one-dimensional, isothermal flow, as shown in Fig. 25. For the case of a Newtonian fluid the governing equations become

$$\frac{\partial V_y}{\partial y'} = 0 \quad (60)$$

$$\frac{\partial P}{\partial y'} = \mu \frac{\partial^2 V_y}{\partial x'^2} \quad (61)$$

$$\text{At } x' = 0, \quad \frac{\partial V_y}{\partial x'} = 0 \quad (62)$$

$$\text{At } x' = W', \quad V_y = 0 \quad (63)$$

The solution of Eqs 61 to 63 for V_y gives

$$V_y = \frac{1}{2\mu} \frac{\partial P}{\partial y'} (x'^2 - W'^2) \quad (64)$$

Making use of Eq 60 implies

$$\frac{\partial^2 P}{\partial y'^2} = 0 \quad (65)$$

Therefore

$$P = C_1 y' + C_2 \quad (66)$$

The two boundary conditions on pressure result from the fact that the pressure at the entrance to the engraved channel (embossing roll surface) is known from the previous calendering analysis in the nip region and that the pressure at the moving free surface is atmospheric. Thus

$$\text{At } y' = 0, \quad P = P_o(t) \quad (67)$$

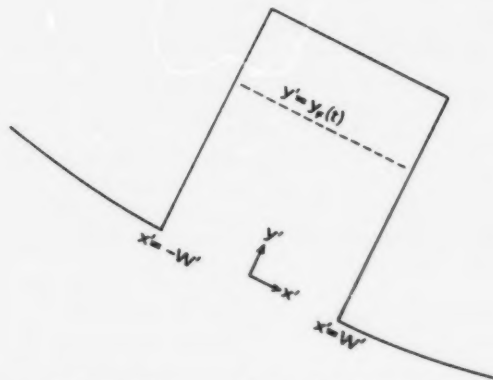


Fig. 25. Schematic diagram of flow in the vicinity of an engraved channel.

$$\text{At } y' = y_F(t), \quad P = P_A \quad (68)$$

Making use of the conditions prescribed by Eqs 67 and 68 gives

$$\frac{P - P_o(t)}{P_A - P_o(t)} = \frac{Y'}{y_F(t)} \quad (69)$$

The flow rate into the engraved channel is readily obtained by integrating Eq 64 as follows

$$\begin{aligned} Q(t) &= \int_{x'=-W'}^{x'=W'} V_y dx' \\ &= \frac{1}{2\mu} \frac{\partial P}{\partial y'} \int_{x'=-W'}^{x'=W'} (x'^2 - W'^2) dx' \quad (70) \\ &= -\frac{2W'^3}{3\mu} \frac{\partial P}{\partial y'} \end{aligned}$$

However, assuming the polymer to be incompressible enables the flow rate to be directly related to the position of the moving melt front as follows

$$Q(t) = 2W' \frac{dy_F(t)}{dt} \quad (71)$$

Therefore, combining Eqs 69 to 71 yields

$$y_F(t) = \left[-\frac{2W'^2}{3\mu} \left(P_A t - \int_0^t P_o(t) dt \right) \right]^{1/2} \quad (72)$$

Equation 72 gives the depth of penetration of material into the engraved channel from a knowledge of the pressure distribution in the nip region. The pressure $P_o(t)$ is directly related to the previously determined pressure distribution $P(x)$ through the fact that

$$t = \frac{x - x_o}{V_1} \quad (73)$$

It should also be noted that this cavity filling analysis can serve as the starting point for the mathematical modeling of the local morphology and microstructure that is developed in the embossed film by means of a similar approach to that taken in injection molding (24).

Power-Law Model

The equation of motion for the steady, isothermal calendaring of a power-law fluid is given by

$$\frac{dP}{dx} = \frac{\partial}{\partial y} \left(K \left| \frac{\partial V_x}{\partial y} \right|^{n-1} \frac{\partial V_x}{\partial y} \right) \quad (74)$$

In the region where the pressure gradient is positive, the velocity profile is given as follows

$$V_x = V + \left(\frac{n}{n+1} \right) \left[\frac{1}{K} \left(\frac{dP}{dx} \right) \right]^{1/n} \left(y^n - h^n \right) \quad (75)$$

and where the pressure gradient is negative the corresponding velocity profile is

$$V_x = V + \left(\frac{n}{n+1} \right) \left[\frac{1}{K} \left| \frac{dP}{dx} \right| \right]^{1/n} \left(h^n - y^n \right) \quad (76)$$

The volumetric flow rate may be obtained by integration of either Eq 75 or 76. Thus

$$Q = 2WVh - \left(\frac{2Wn}{2n+1} \right) \left[\frac{1}{K} \left(\frac{dP}{dx} \right) \right]^{1/n} h^{\frac{2n+1}{n}} \quad (77)$$

The pressure gradient is readily determined from Eq 77 as follows

$$\frac{dP}{dx} = K \left[\left(\frac{2n+1}{2Wn} \right) \left(\frac{2WVh - Q}{h^{\frac{2n+1}{n}}} \right) \right]^n \quad (78)$$

The pressure distribution is then determined from numerical integration of Eq 78. If the upstream pressure at $x = x_o$ is P_o the pressure distribution is given by

$$P = P_o + K \left(\frac{2n+1}{2Wn} \right)^n \int_{x=x_o}^{x=x} \left(\frac{2WVh - Q}{h^{\frac{2n+1}{n}}} \right)^n dx \quad (79)$$

The local deformation analysis in the region of the engraved channel for the power-law fluid is exactly analogous to the preceding Newtonian case. For the power-law fluid, the corresponding velocity and pressure distributions are given as follows

$$V_y = \left(\frac{n}{n+1} \right) \left(\frac{1}{K} \frac{\partial P}{\partial y'} \right)^{1/n} \left(W'^{\frac{n+1}{n}} - x'^{\frac{n+1}{n}} \right) \quad (80)$$

$$\frac{P - P_o(t)}{P_A - P_o(t)} = \frac{y'}{y_F(t)} \quad (81)$$

The flow rate is therefore given by

$$\begin{aligned} Q(t) &= 2W' \frac{dy_F(t)}{dt} \\ &= \int_{x'=-W'}^{x'=W'} V_y dx' \quad (82) \\ &= \left(\frac{2n}{2n+1} \right) \left(\frac{W'^{2n+1}}{K} \frac{\partial P}{\partial y'} \right)^{1/n} \end{aligned}$$

Combining Eqs 81 and 82 yields

$$\begin{aligned} y_F(t) &= \frac{W'}{K^{1/(n+1)}} \left[\left(\frac{n+1}{2n+1} \right) \int_0^t (P_o(t) - P_A)^{1/n} dt \right]^{n/(n+1)} \quad (83) \end{aligned}$$

Although this mathematical model of the embossing nip region may appear to be somewhat crude and not a realistic representation of the physics of the process, the following justifications are given. From the point of view of the material, the polymer is squeezed in traveling through the nip region, which develops an elevated pressure causing the material to flow into the

engraved channel. This is to some extent analogous to the case of molten polymer contained in the nozzle of an injection molding machine. The resulting mathematical model is computationally simple and can be readily tested. For these reasons it is considered warranted for a preliminary engineering analysis of the embossing dynamics.

COOLING ZONE

During the short interval when the film is in contact with both embossing rolls, heat is generated by viscous dissipation and lost through direct contact with the cool embossing roll surfaces. The embossing step is thus inherently nonisothermal, but due to the complexity of the analysis and the short duration of contact with both roll surfaces the previous analysis has considered the process as being isothermal. However, the polymer film typically remains in contact with one of the cool embossing roll surfaces after emerging from the nip region. In this situation the heat transfer analysis is exactly similar to that for the preheat roll and will not be repeated here. It can be assumed that the temperature of the polymer film will be very close to the temperature of the embossing roll once the film is completely detached from the embossing roll surface. Subsequently, the free moving film exchanges heat through convection with the environment until it reaches the wind-up roll. Typically, the travel distance is of the order of several meters. Erickson, *et al.* (25) have developed an approach for determining the surface temperature distribution along a freely-moving continuous sheet. If the polymer film has not attained a temperature close to that of the environment while being wound, significant stress levels could develop in the film, particularly in the tightly wound central core region where the material is constrained. These details are not considered within the scope of the present treatment.

CONCLUSIONS

A preliminary engineering analysis of the dynamics and heat transfer of the film embossing process has been given by employing suitably simplified mathematical models. The thermal and stress fields have been decoupled and analyzed separately. Experimental data have been measured in order to validate some of the underlying assumptions, to provide specification of boundary conditions, and to evaluate the predictive ability of the mathematical models.

In general, the theoretical treatment provides a reasonable description of the thermal history of the film prior to the nip region of the embossing rolls. Experimental measurements are required in order to properly test the validity of the dynamic analysis. Additional work is also required to predict the air temperature distribution in the vicinity of the radiation heaters.

Despite the above-mentioned shortcomings, the suggested mathematical model can be usefully employed for determining the trends on relative effects of changes in operating conditions, material properties, or design variables.

REFERENCES

1. A. Haber and M. R. Kamal, paper presented at 33rd C.S.Ch.E. Conference, Toronto, Ontario, October 5, 1983.
2. H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Second Edition, Oxford University Press, New York (1959).
3. B. Carnahan, H. A. Luther, and J. O. Wilkes, "Applied Numerical Methods," John Wiley & Sons, New York (1969).
4. "Transient Heating of a Film in a Combined Mode," Technical Report, Union Carbide Corporation (1971).
5. G. Menges and W. O. Predohl, *Soc. Plastics Engrs. Tech. Papers*, 18, 717 (1972).
6. J. P. Holman, "Heat Transfer," Fourth Edition, McGraw-Hill Book Company, New York (1976).
7. E. M. Sparrow and R. D. Cess, "Radiation Heat Transfer," Third Edition, Hemisphere Publishing Corp., Belmont, California (1978).
8. J. M. McKelvey, "Polymer Processing," John Wiley & Sons, New York (1962).
9. S. Middleman, "Fundamentals of Polymer Processing," McGraw-Hill Book Company, New York (1977).
10. Z. Tadmor and C. G. Gogos, "Principles of Polymer Processing," John Wiley & Sons, New York (1979).
11. R. E. Gaskell, *J. Appl. Mech.*, 17, 334 (1950).
12. I. Brazinsky, H. F. Cosway, C. F. Valle, Jr., R. Jones, R. Clark, and V. Story, *J. Appl. Polym. Sci.*, 14, 2771 (1970).
13. W. W. Alston and K. N. Astill, *J. Appl. Polym. Sci.*, 17, 3157 (1973).
14. P. R. Paslay, *J. Appl. Mech.*, 24, 602 (1957).
15. J. S. Chong, *J. Appl. Polym. Sci.*, 12, 191 (1968).
16. M. Finston, *J. Appl. Mech.*, 18, 12 (1951).
17. R. Takserman-Krozer, G. Schenkel, and G. Ehrmann, *Rheol. Acta*, 14, 1066 (1975).
18. N. G. Bekin, V. V. Litvinov, and V. Yu-Petrusanskii, *Intl. Polym. Sci. Technol.*, 3, T-55 (1976).
19. C. Kiparissides and J. Vlachopoulos, *Polym. Eng. Sci.*, 16, 712 (1976).
20. C. Kiparissides and J. Vlachopoulos, *Polym. Eng. Sci.*, 18, 210 (1978).
21. E. Mitsoulis, J. Vlachopoulos, and F. A. Mirza, *Polym. Eng. Sci.*, submitted for publication.
22. J. Vlachopoulos and E. Mitsoulis, "Adv. Transport Processes," submitted for publication.
23. G. Ehrmann and J. Vlachopoulos, *Rheol. Acta*, 14, 761 (1975).
24. M. R. Kamal and P. G. Lafleur, *Soc. Plastics Engrs. Tech. Papers*, 29, 386 (1983).
25. L. E. Erickson, L. A. Cha, and L. T. Fan, *Chem. Eng. Prog. Symp. Series*, 62, No. 64, 157 (1966).

NOMENCLATURE

- | | |
|-----------|--|
| A | = Amplitude of sinusoidal function defining embossing surface. |
| c_p | = Heat capacity at constant pressure. |
| c_v | = Heat capacity at constant volume. |
| C_1 | = Integration constant. |
| C_2 | = Integration constant. |
| F | = Shape factor; force tending to separate embossing rolls. |
| $f(y, z)$ | = Arbitrary function of y and z . |
| $f_1(y)$ | = Arbitrary function of y . |
| $g(x, z)$ | = Arbitrary function of x and z . |
| $g(z, t)$ | = Arbitrary function of z and t . |
| h | = Convective heat transfer coefficient; vertical distance to embossing roll surface. |
| h_1 | = Vertical distance to embossing roll surface. |
| h_2 | = Vertical distance to backup roll surface. |
| H | = Film thickness. |
| H_0 | = Gap separation. |
| k | = Thermal conductivity. |
| K | = Parameter in power-law model. |

L	= Distance between center of embossing roll and center of backup roll.
L_t	= Travel length.
n	= Power-law exponent.
p	= Pressure.
P_A	= Atmospheric pressure.
P_{max}	= Maximum pressure for Newtonian calendaring for $X_D/\sqrt{2R_1H_0} = 0.475$.
P_o	= Pressure at position x_o .
$P_o(t)$	= Pressure at entrance of the engraved channel.
Q	= Volumetric flow.
R	= Radius of roll.
R_{a1}	= Radial distance to embossing roll surface.
R_{a2}	= Radial distance to backup roll surface.
R_1	= Radius of embossing roll.
R_2	= Radius of backup roll.
t	= Time.
t_c	= Contact time with preheat roll surface.
t^*	= Dimensionless time, t/t_c .
T	= Temperature.
T_A	= Ambient temperature.
T_p	= Set temperature of preheat roll.
T_R	= Radiation heater temperature.
T^*	= Dimensionless temperature, $(T - T_A)/(T_p - T_A)$.
v_x	= Velocity component in x -direction.
v_y	= Velocity component in y -direction.
V	= Film velocity or take-up speed.
V_1	= Velocity of embossing roll surface.
V_2	= Velocity of backup roll surface.
w	= Half width of film.
W	= Film width.
W'	= Half width of engraved channel.
$\dot{W}$	= Power input to the material by the embossing rolls.
x	= Spatial coordinate.
x_o	= Spatial position; attachment point.
x_D	= Detachment point.
x'	= Local spatial coordinate for incomplete contact analysis.
x^*	= Dimensionless distance, x/L_t .
y	= Spatial coordinate.
$y_F(t)$	= Position of polymer surface within engraved channel.
y'	= Local spatial coordinate for incomplete contact analysis.
y^*	= Dimensionless position, y/H .
z	= Spatial coordinate.
z^*	= Dimensionless position, z/W .
ΔT	= Adiabatic temperature rise.
$\dot{\mathbf{A}}$	= Rate of deformation tensor.
ϵ	= Emissivity of the polymer.
ϵ_1	= Height of surface feature on embossing roll.
ϵ_2	= Height of surface feature on backup roll.
θ	= Angular position relative to vertical reference.
μ	= Newtonian viscosity.
ρ	= Density.
σ	= Stefan-Boltzmann constant.
τ_{ij}	= Stress tensor component.
$\underline{\tau}$	= Stress tensor.
ω_1	= Angular velocity of embossing roll.

ω_2	= Angular velocity of backup roll.
D/DT	= Material or substantial derivative.
Π_{Δ}	= Second scalar invariant of the rate of deformation tensor.

APPENDIX

The results shown in Figs. 5, 6, 7, 8, 9, 10, 11, 14, and 15 were obtained for the following conditions:

Film velocity	0.21 m/s
Film thickness	0.0000633 m
Film width	0.8128 m
Travel length between preheat roll and embossing roll	0.47 m
Ambient temperature	25°C
Initial film temperature	31.6°C
Preheat roll temperature	93.3°C
Temperature of radiation heaters	800°C
Preheat roll diameter	0.29 m

The results shown in Figs. 20, 21, 22, and 23 were obtained for the following conditions unless otherwise noted:

Embossing roll surface	$R_{a1} = R_1 + A \sin[8(\theta - wt)]$
Separation between roll centers	0.1534 m
Radius of embossing roll	0.0762 m
Radius of backup roll	0.0762 m
rpm of embossing roll	26.317
rpm of backup roll	26.317
Amplitude of sinusoidal surface (A)	0.0001 m
Film width	0.508 m
Melt viscosity	10000 Pa-s

DISCUSSION: M. R. KAMAL, A. HABER, AND M. E. RYAN

E. Mitsoulis: When the film passes through the two cylinders, does it form any melt bank at the entrance?

M. E. Ryan: No, in our case we do not have a melt bank buildup in the embossing zone for these thin films. However, there are embossing operations, such as cast extrusion embossing, where you build up a melt bank, as in calendaring, but there you are embossing a thicker molten sheet.

E. Mitsoulis: Do you know the location of the detachment point?

M. E. Ryan: This can be precisely calculated from the mathematical model. However, experimentally we have not been able to measure the detachment point. We are hoping to do the measurement precisely.

E. Mitsoulis: Can you obtain the pressure distribution in the nip?

M. E. Ryan: Yes, you can calculate the pressure distribution, material flow rate, and film thickness or the physical dimensions of the embossed film. In

addition to the ultimate properties, the physical dimensions of the embossed film provide a means of testing the validity of the model.

J. Wallace: I was slightly puzzled by the drawings that show the thickness of the film decreasing very markedly as the embosser passes over. In the extreme case, the thickness of the film might not change at all.

M. E. Ryan: Experimentally, in our case, the change in film thickness is very small. In our particular situation, the variations due to the embossed pattern may be large but the actual change in the film thickness is slight. The schematics were not drawn to scale in terms of our experimental studies and they may be somewhat misleading.

J. Wallace: What is the temperature of the embossing roll?

M. E. Ryan: The embossing roll is water cooled and the temperature of the film at the point of contact with the embossing roll is around 100°C.

J. Wallace: If the preheat roll analysis applies equally to the embossing roll, the film will be rapidly cooled and the film may be deformed against the moving backup roll.

M. E. Ryan: I would not disagree with you on this point. The same heat transfer analysis for the preheat roll can be applied to the embossing roll, which indicates solidification of the embossed film by the time the film detaches. The proper way of analyzing this situation is more in terms of a cold forming approach. This is what we are currently working on. Our attempt with the calendering analogy is to explore whether that approach has any merit at all. Does it provide any useful predictive ability? If it does, it might be of utility even if we don't have the physics quite correct. It may turn out to be poor in this situation and that is why we are working on the development of a cold forming approach to model the process. However, the model proposed here should be quite applicable to the matte finish or cast extrusion embossing processes where the material is in a molten state. It appears that these operations are becoming technologically more important for high speed embossing processing.

H. Winter: Your model should be very valid for the embossing of a thick sheet where one surface is embossed and one side remains smooth. However,

if the rubber backup roll is significantly deformed during the short instant of contact such that the film is embossed on both sides or squeezed by the two surfaces, then the model may have to be modified.

M. E. Ryan: In our case, even for these thin films, only one side is embossed and the other side effectively remains smooth. However, the deformation of the embossing rolls, particularly the rubber backup roll, is an important problem which we are looking into more deeply. There is quite an extensive literature related to this particular problem, which we hope to apply to the embossing situation.

A. Fisher: Do you plan to look at the temperature variation across the sheet on the duplication of the pattern or on the physical properties of the film?

M. R. Kamal: Ideally we would like to continue this work in these directions. Clearly one can not get very far without taking into consideration the non-isothermal nature of the process. The microstructural and ultimate property analyses require a knowledge of the stress and temperature field throughout the film.

A. Fisher: Have you done any work or are you intending to do any work where you emboss two layers at once rather than just one layer?

M. E. Ryan: As far as the mathematical model is concerned we can probably handle two layers without any difficulty, although we have not made any calculations for this situation. Experimentally, for two or more layers one may encounter practical difficulties in separating the film after embossing.

P. J. Carreau: I was surprised by the values that were used for the view factor, which seems very low considering that the radiation heaters have a surrounding cover and there should be radiation reflected from the cover giving a view factor when the film is directly opposite closer to unity. Then the radiation heat transfer would be more important than the contribution due to convection.

M. E. Ryan: The cover around the radiation heaters is a grey insulator and is not a reflective surface. Although it does reradiate, this was not included in the analysis. The view factor was calculated only from the cylindrical tubes, neglecting the cover. This may not be a good assumption and we should perhaps examine this question more rigorously.

Evaluation of Simple Dynamic Models and Controllers for Hydraulic and Nozzle Pressure in Injection Molding

DIB ABU FARA, M. R. KAMAL*, and W. I. PATTERSON

*Department of Chemical Engineering
McGill University
Montreal, Canada H3A 2A7*

Simple pseudo-steady state relations between the hydraulic and nozzle pressures of an injection molding machine were presented and verified experimentally. A simulation study was performed to evaluate the performance of simple controllers using dynamic models developed for the hydraulic and nozzle pressures. The controllers chosen were the discrete proportional, proportional-integral (PI), and proportional-integral-derivative (PID) types, tuned according to the ITAE criterion. The control of hydraulic pressure simulation showed that the PI controller had the best overall performance, whereas the result of nozzle pressure control loop simulation showed that the PID controller performance was better than that of the PI controller. All the controllers, in both loops, gave responses that were about an order of magnitude more rapid than the open loop response.

INTRODUCTION

The injection molding of thermoplastics is a multivariable process involving complex interactions between material characteristics and the molding conditions to obtain the desired properties of the molded article. It is necessary to understand these interactions in order to control the changes that occur during the injection molding cycle, both in the process and the product. Process control is a tool for achieving improved production economics by the minimization of waste and product variability and improving the quality of the molded article.

This work explores the use of some simple phenomenological relationships involving different important variables for controlling some important parameters of the injection molding process. These relationships are of the form of pseudo-steady state and dynamic models.

GENERAL BACKGROUND

Modeling and Control

Steady-state models are important for understanding the fundamental behavior of a process and the effects of different process variables. Dynamic models describe the time-varying, or unsteady-state responses, of the product properties or process variables to manipulated changes of certain variables or disturbances external to the process.

It is the goal of an automatic control system to force the process to follow the desired change in

operating conditions or to reject the disturbances, or both. The rational design of a control loop, therefore, requires an accurate dynamic model of the behavior of the process variable that is to be controlled. These models can be obtained by either theoretical analysis or experimentation. Dynamic models are derived theoretically by applying the momentum, energy, and mass balances together with the necessary equations of state and constitutive relations. The solution of the resulting partial differential equations usually demands considerable computational effort. Theoretically obtained dynamic models are thus poorly suited for process control purposes.

The practical application of control theory, consequently, relies on simpler dynamic models based on an experimental or transfer function approach. This approach applies a controlled variation to a process input and the resultant response is measured as illustrated in Fig. 1. The transfer function is obtained from the ratio of the output to the input, often transformed by the Laplace or Fourier techniques. This method suffers from two disadvantages: the process must be physically tested to obtain the necessary data, and there is the implicit assumption that the process is linear. It is therefore necessary to determine the limits of the validity of the second assumption. This means that, in practice, a number of experiments larger than the minimum required to obtain the transfer function must be carried out, since the complete operating range of the process has to be explored experimentally. The transfer function approach, however, gives signifi-

* To whom all correspondence regarding this manuscript should be addressed.

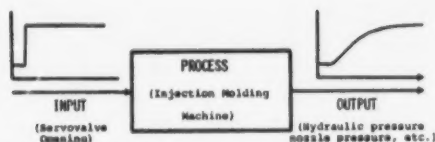


Fig. 1. Transfer function representation of a process.

cantly simpler models than those of the transport phenomena approach, and they are well suited for process control applications.

Identification Techniques

The experimental procedure and the analysis of the dynamic behavior of processes from the input and output signals is called system identification and has been extensively studied in recent years. This activity is reflected in the survey papers published by Astrom and Eykhoff (1), Nieman, *et al.* (2), and Gustavsson (3). The technique chosen for system identification depends on the goal of the process model. The goal, typically, is one of the following: the verification of theoretical models, adjustment of the controller parameters, control algorithm design, implementing self-tuning control, or process failure detection. The purpose of identification is often to develop a model that describes the process adequately and can be used to design a control system for that process.

Classically, the engineering methods for estimating a transfer function model are based on a deterministic perturbation of the input. The perturbation usually chosen is either a step, pulse, or sinusoid, although others have been suggested (4 to 6). The step function is the most widely used, since it is easy to generate and the response can be qualitatively checked for physical correctness. The pulse input requires considerably more computational processing and the results are susceptible to contamination by the always present process noise. Sine-wave testing demands many experiments at different exciting frequencies to elucidate the transfer function (4). When step testing is used, the size of the step should be chosen with some care. It must be sufficiently large that the response can be distinguished from the process noise, but small enough that the linearity assumption is not violated.

The disadvantage of deterministic tests is that their results are useful only when the response to noise ratio is large and the other variables affecting the process do not change appreciably. Moreover, it is usually difficult to discriminate between models of second and third or higher orders, so that, in practice, some features of the process may not be adequately described.

Statistical approaches (often called "stochastic identification") have been developed recently (7, 8) which, after treatment of the measured response, permit the determination of the transfer function and the description of the noise associated with the process. The estimates of the process model are therefore more reliable.

The input-output relationships obtained by the

stochastic approach are often called parametric models and are of the form (7):

$$Y(k)(1 - \delta_1 B - \delta_2 B^2 - \dots - \delta_r B^r) = (\omega_0 - \omega_1 B - \omega_2 B^2 - \dots - \omega_s B^s)X(k - b) + N(k) \quad (1)$$

or

$$Y(k) = \frac{\omega_s(B)}{\delta_r(B)} X(k - b) + \frac{\theta_q(B)}{\phi_p(B)} a(k) \quad (2)$$

where

$Y(k)$ = The output at the k^{th} measurement.

$X(k - b)$ = The input at $(k - b)^{\text{th}}$ measurement.

$N(k)$ = The noise at k^{th} measurement.

B = The backwards operator; $BY(k) = Y(k - 1)$.

b = Number of lags.

$\omega_s(B)$ = $(\omega_0 - \omega_1 B - \omega_2 B^2 - \dots - \omega_s B^s)$.

$\delta_r(B)$ = $(1 - \delta_1 B - \delta_2 B^2 - \dots - \delta_r B^r)$.

$\theta_q(B)$ = $(1 - \theta_1 B - \theta_2 B^2 - \dots - \theta_q B^q)$.

$\phi_p(B)$ = $(1 - \phi_1 B - \phi_2 B^2 - \dots - \phi_p B^p)$.

$a(k)$ = White noise (i.e. a random disturbance).

$\delta_1, \delta_2, \dots$, and $\omega_0, \omega_1, \omega_2, \dots$ are parameters obtained from the analysis of the experimental data.

Stochastic identification methods may be classified according to their use as either off-line or on-line. The off-line methods collect the response data for later analysis, whereas the on-line methods estimate new process model parameter values each time a measurement is made. The off-line methods are generally more powerful and require more computation. The rest of this section will give a brief description of the off-line identification method systematized by Box and Jenkins (7), which yields a parametric model.

This method is well suited to determine the model order (or number of parameters), the time delay, and parameter values for unknown processes. It is an iterative procedure, as shown in Fig. 2, and consists of three main steps: identification of the order of the transfer function and noise model; estimation of the model parameter values; and diagnostic verification of the model.

The basic tools employed in the identification step are the cross correlation of the input and output and the process impulse response. To illustrate this, Eq 1 can be rewritten as:

$$Y(k) = (V_0 + V_1 B + V_2 B^2 + \dots + V_n B^n)X(k - b) + N(k) \quad (3)$$

or

$$Y(k) = V(B)X(k - b) + N(k) \quad (4)$$

where $V_0, V_1, V_2, \dots, V_n$ are the impulse response weights of the system at discrete time intervals, $t_0, t_1, t_2, \dots, t_n$. The observed pattern of the estimated impulse weights is then used to choose a probable transfer function model, $\omega_s(B)/\delta_r(B)$, i.e. to estimate the values of s and r in the polynomials, $\omega_s(B)$ and $\delta_r(B)$ (7). The noise term $N(k)$ in Eq 1 then can be written in terms of the tentative transfer function model. The autocorrelation and partial autocorre-

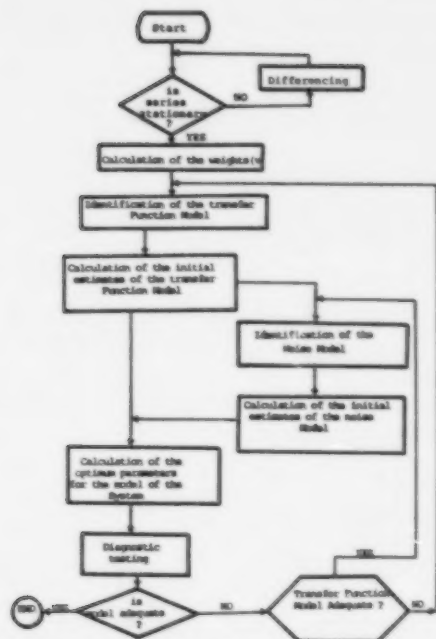


Fig. 2. Flow chart of the Box and Jenkins Method.

lation functions of the residuals are then used to identify the noise model, i.e. to estimate the values of q and p of the term $\theta_q(B)/\phi_p(B)$ in Eq 2.

The tentative models of the transfer function and noise are used to obtain the best estimates of the parameters ω , δ , θ , and ϕ by minimizing the sum of squares of the difference between the data and the model predictions (7), using the maximum likelihood approach:

$$S(\omega, \delta, \theta, \Phi) = \sum_{k=1}^n a^2(\omega, \delta, \theta, \Phi) \quad (5)$$

The process plus noise models are then tested for statistical adequacy. If they are statistically adequate, the residual differences are purely random; if not, the difference pattern is used to modify the models in a second iteration. The identification is repeated in an iterative manner until statistically adequate models are found.

Controllers

A generalized closed-loop control system can be represented by the block diagram shown in Fig. 3a. The set-point is the desired value of the controlled variable and may vary in a time-dependent manner. The measured value of the controlled variable is compared to the set-point value and the difference, or error, is the input signal to the controller. The controller thus acts upon the error and produces a change in the output signal sent to the process actuator such that the error will be diminished. The relationship between the error input and the corrective output depends on the type of controller installed. The simplest type is the proportional controller represented by Eq 6 below (4):

$$M = k_c \cdot e + bias \quad (6)$$

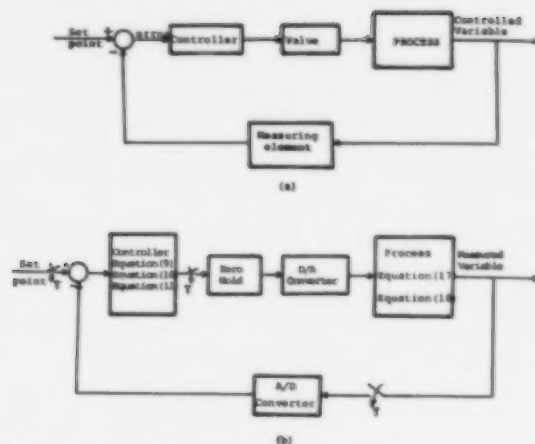


Fig. 3. Closed-loop block diagram (a) General closed-loop control system; (b) Simulation control loop for Hydraulic and Nozzle pressures.

where

M = The controller output, or manipulated variable.

k_c = The controller gain.

e = The error.

$bias$ = A constant signal to drive the actuator when the error is zero.

A main disadvantage of the proportional controller is a steady-state error or offset generated when the set-point is changed. This offset can be eliminated if a proportional-integral (PI) controller is used. This mode of control is described by the relationship:

$$M = k_c \cdot e + \frac{k_c}{\tau_I} \int_0^t e dt + bias \quad (7)$$

where τ_I is the integral or reset time constant. Equation 7 shows that in addition to the proportional action term, $k_c \cdot e$, a term which is proportional to the integral of the error is present. The advantage of the integral action in eliminating the offset is balanced by the disadvantage of a more oscillatory behavior of the controlled variable. The offset can often be eliminated and the oscillation reduced by the addition of a derivative action to the PI controller to give a proportional-integral-derivative (PID) controller. The PID controller is represented by the equation:

$$M = k_c \cdot e + \frac{k_c}{\tau_I} \int_0^t e dt + k_c \tau_D \left(\frac{de}{dt} \right) + bias \quad (8)$$

where τ_D is the derivative time constant or rate time.

The selection of the control system depends upon the particular application. If an offset is acceptable, the proportional controller would likely be selected, since it is the simplest and the easiest to implement. Otherwise a PI or a PID controller would be selected depending on the tolerable degree of oscillation. PID control is particularly suited to situations where rapid and frequent external disturbances enter the process.

The discrete equivalent forms of the continuous controllers are used in digital computer process control. The discrete form of the proportional controller can be represented as (9):

$$M(k) = k_r[e(k) - e(k-1)] + M(k-1) \quad (9)$$

where k is the sampling instant and the argument, $(k-1)$, is the value of the variable at the previous sampling time. The discrete form of the PI controller is derived by replacing the integral in Eq 7 by the sum using the rectangular integration rule to give (9):

$$M(k) = k_r[e(k) - e(k-1)] + (T/\tau_i)e(k) + M(k-1) \quad (10)$$

where T is the sampling time. The discrete PID controller is obtained by replacing the integral in Eq 8 by a sum and the derivative by a finite difference. Writing Eq 8 for the k and $(k-1)$ times and obtaining the difference gives the recursive form of the controller (9):

$$M(k) = k_r \left[\{e(k) - e(k-1)\} + \frac{T}{\tau_i} e(k) + \left(\frac{\tau_D}{T} \right) \{e(k) - 2e(k-1) + e(k-2)\} \right] + M(k-1) \quad (11)$$

Controller Tuning

A critical phase of the implementation of any controller is determining the values of its parameters. In addition, the digital controller needs to have a sampling period specified. This process has as its objective the selection of a combination of controller parameters that gives a satisfactory response according to the appropriate criteria. The criteria used to select the best response vary depending on the application and the process. The commonly used criteria can be classified into two categories: simple criteria based on a single response characteristic, and more exact criteria based on the entire response.

An example of the first is the 1 to 4 decay ratio (10), while an example of the second is the integral of time multiplied by the absolute value of the error (ITAE) (9).

The general form of the integral criteria is:

$$I = \int_0^\infty f(t, e(t)) dt \quad (12)$$

The integral criteria give values for the parameters of the control algorithm that minimize the value of the selected integral criterion for the response of the system to a selected input.

THE APPLICATION OF MODELING AND CONTROL TO INJECTION MOLDING

The study of the injection molding of thermoplastics has received considerable attention in recent years. A number of studies have been concerned with the phenomenological modeling of various phases of the injection molding process. Dif-

ferent models of varying complexity, depending on the simplifying assumptions and the nature of the rheological constitutive equations and other relationships, have been proposed (11 to 18). The models and experimental data represent attempts to predict the distributions of polymer pressure, temperature, and velocity in the cavity and their dependence on resin properties, cavity shape, and molding conditions. Some of these models can also yield information regarding the relationships between resin properties, molding conditions, the thermo-mechanical history of the resin, and the ultimate properties of the molded article.

These studies, without exception, require the numerical solution of the model equations, which is obtained only after extensive computation and is usually restricted to steady-state operation. Process control, however, needs simple empirical or theoretical models (relationships) that can be solved rapidly on small computers. Such models should relate the time-varying distributions of process parameters like pressure, temperature, or velocity to the relevant machine and material variables.

Shankar and Paul (19) developed deterministic models for the injection, packing, and cooling stages of the injection process by employing the equation of conservation of mass, momentum, and energy for the oil in the hydraulic injection cylinder, the polymer melt in the barrel, and the polymer in the mold cavity. The dynamic behavior of the injection phase was described by a set of seventh order nonlinear equations. The Model predictions were in qualitative agreement with experimental data. However, a large difference between the predicted and experimental cavity pressures was noted and attributed to the assumption of isothermal polymer melt flow in the cavity.

Pseudo-Steady State Study

Several workers have attempted to develop descriptive (functional) relationships between the injection molding variables (20 to 24). Figure 4 shows

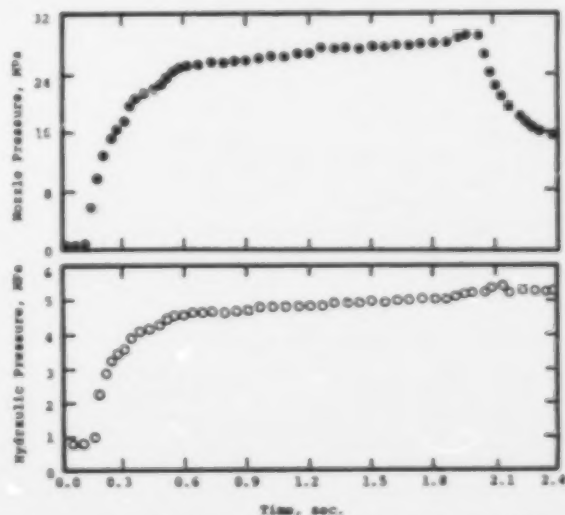


Fig. 4. Typical hydraulic and nozzle pressure-time profiles.

typical hydraulic pressure and nozzle pressure profiles. It is obvious that the nozzle pressure-time profile closely follows the hydraulic pressure-time profile throughout the injection phase. This observation precipitated the idea of deriving a quantitative relation between the two variables, which might be useful for control purposes. For example, if it is desired to control nozzle pressure and a simple dynamic relation between nozzle and hydraulic pressures could be obtained, then it might be preferable to directly control hydraulic pressure, since the latter is a more fundamental machine variable and it is easier to measure.

Kamal, Patterson, and Abu Fara (25) have examined the relationship between nozzle pressure and hydraulic pressure using two approaches. The first approach is based on a simplified theoretical analysis of the interactions between the hydraulic pressure and the injection molding variables, while the second is an empirical analysis of experimental data. A detailed description of the experimental apparatus used in the study is available elsewhere (26, 27).

The simplified theoretical analysis of the injection phase has been based on a force balance applied to the injection ram shown in Fig. 5a. Nozzle pressure is related to hydraulic pressure by the equation:

$$P_N = \frac{A_p}{A_f} P_H - \frac{F_s}{A_f} \quad (13)$$

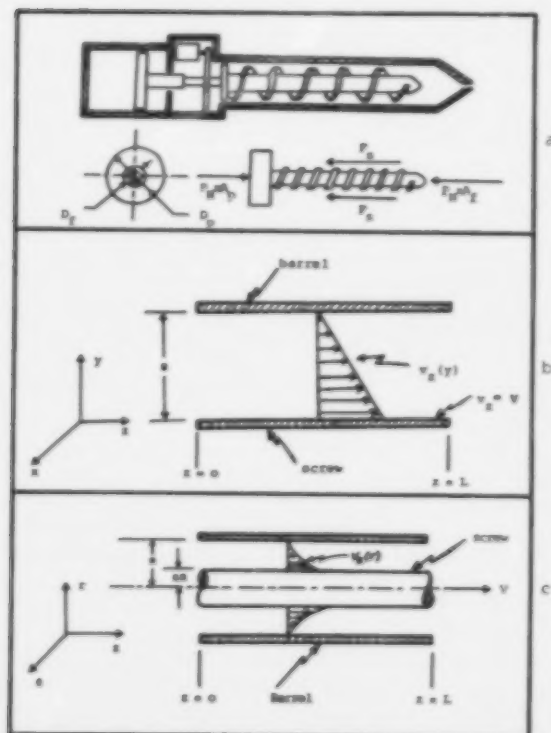


Fig. 5. Modeling of the injection cylinder and screw: (a) Force balance; (b) Drag flow between two horizontal planes; and (c) Drag flow between two concentric horizontal cylinders.

where:

P_N = Nozzle pressure, Pa.

P_H = Hydraulic pressure, Pa.

A_p = Cross-sectional area of the ram piston, m^2 .

A_f = Cross-sectional area of the screw flight, m^2 .

F_s = Shear force exerted by the polymer on the screw, N.

The shear force, F_s , was estimated from the equations of change (29) using the plane couette flow (PCF) and the axial annular couette flow (ACF) approximations, as shown in Figs. 5b and 5c respectively, which gave the following two formulas for the shear force (25):

PCF:

$$F_s = -\pi M \left(\frac{V}{B} \right)^n D_f L \quad (14)$$

ACF:

$$F_s = \frac{2\pi ML}{R^{n-1}} \left[\frac{V}{S(K^{1/n} - 1)} \right]^n \quad (15)$$

where:

F_s = Shear force, N.

M, n = The parameters of the power-law viscosity relationship.

V = Injection velocity, m/sec.

D_f = Flight diameter, m.

L = Screw length, m.

R = Inside barrel radius, m.

K = Ratio of flight radius to the inside barrel radius, $K < 1$.

$S = n/(n-1)$.

Figure 6 shows the calculated nozzle pressure for the two approaches together with the experimental data for different injection velocities and barrel temperatures. The model predictions are in good agreement with the experimental data. The difference between the experimental and calculated values would be smaller, if better rheological data were available.

Although the ACF model is a more realistic representation of the physical situation, the PCF model yields almost identical results. This is explained by the small gap ($K \approx 1$) between the screw flights and the barrel, which justifies the use of the simple formula (Eq 14) of the parallel plate model.

The theoretical relationship, Eq 13, was substan-

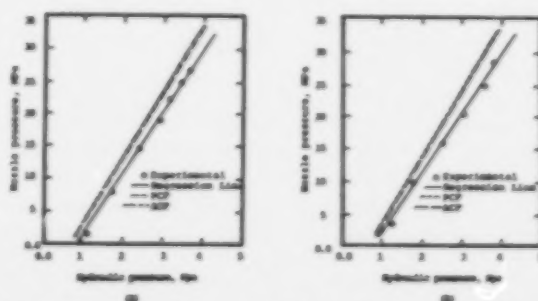


Fig. 6. Experimental and calculated nozzle pressure as a function of hydraulic pressure for resin Ex2; (a) Barrel temperature = 215°C, injection velocity = 1.9×10^{-3} m/s.; (b) Barrel temperature = 232°C, injection velocity = 2×10^{-3} m/s.

tiated by an empirical relationship obtained by linear regression of the experimental data. Nozzle pressure was related to the hydraulic pressure by:

$$P_N = k_1 \cdot P_H + k_2 \quad (16)$$

where:

k_1 = Slope of the regression line, dimensionless.

k_2 = Intercept with the ordinate, Pa.

The values for k_1 and k_2 are given in Table 1, which also shows that the coefficients of correlation are 0.98 or better. Figure 7 shows the relation between nozzle and hydraulic pressures for different valve openings. These results show that the relation between nozzle pressure and hydraulic pressure is linear for a wide range of operating conditions.

The pseudo-steady state relationships, although useful in examining the interactions between the process variables, do not reflect the dynamic effects that result when the process variables are changing in response to a time-variable forcing function. Complete dynamic models are thus required to furnish the basic information needed to develop dependable control strategies for the injection molding process.

Table 1. Regression Coefficients for $P_N - P_H$

Valve Opening %	K1	K2 MPa	Coefficient of Correlation
25	7.05	-0.53	0.98
37	7.26	-1.55	0.99
50	7.76	-2.73	0.99
62	7.94	-3.37	0.99

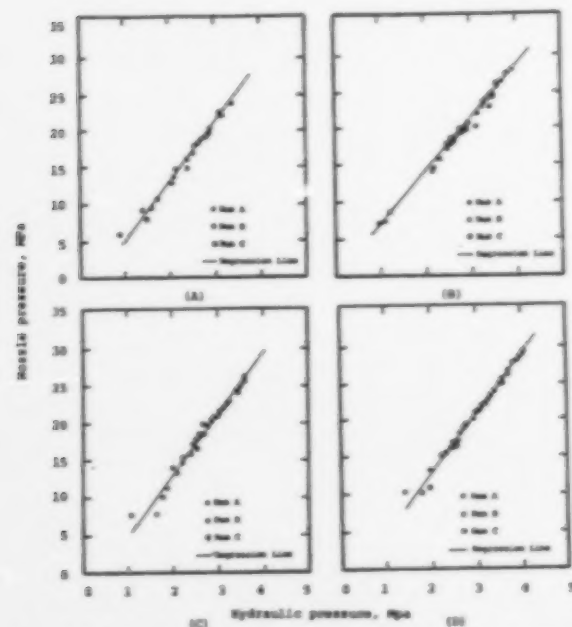


Fig. 7. Relation between nozzle pressure and hydraulic pressure (a) 25 percent, (b) 37 percent, (c) 50 percent, (d) 62 percent valve opening.

Dynamic Study

Kamal, *et al.* (30) studied the dynamics of the injection molding process using the same injection molding machine. Deterministic (step) and stochastic (PRBS) input functions of the manipulated variable (servovalve opening) were used in this study. They developed dynamic models, in the form of transfer functions, relating the variation in the servovalve opening to variations in the hydraulic pressure and nozzle pressure.

The hydraulic pressure response was best modeled by a delayed first order plus oscillatory component, as given by:

$$P_H = G(1 - e^{-(t-D)/\tau}) + G_1 \left[\frac{1}{(1 - \xi^2)^{1/2} \tau_1} \cdot e^{-t/\tau_1} \sin \left\{ (1 - \xi^2)^{1/2} \frac{t}{\tau_1} \right\} \right] \quad (17)$$

where:

P_H = Hydraulic pressure, Pa.

G, G_1 = Process gains, Pa/% change in valve opening.

τ, τ_1 = Time constants, sec.

D = Time delay, sec.

ξ = Damping factor, dimensionless.

The first term of Eq 17 accounts for the delayed first order part of the response, while the second term is the oscillatory, servovalve-induced component. Figure 8a shows good agreement between the model, Eq 17, and experimental data.

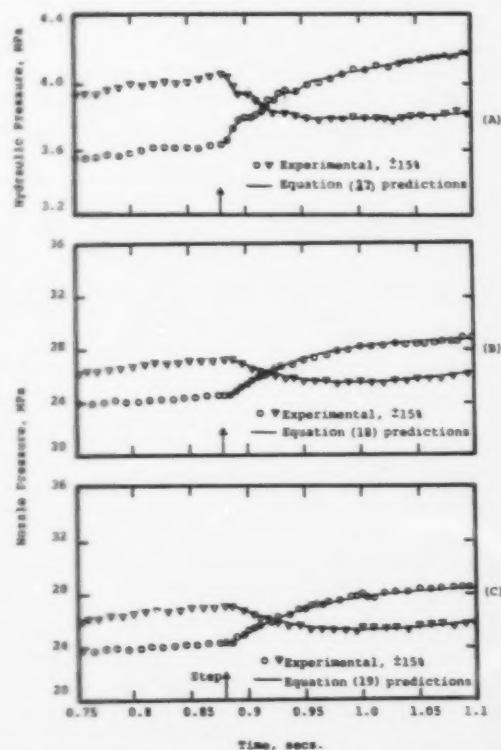


Fig. 8. Comparison of experimental hydraulic and nozzle pressure responses to fitted models.

A first order plus time delay and an overdamped second order model were fitted to the nozzle pressure response as:

First order:

$$P_N = G(1 - e^{-(t-D)/\tau}) \quad (18)$$

second order:

$$P_N = G \left[1 - \frac{\tau_1 \tau_2}{\tau_1 - \tau_2} \left\{ \frac{1}{\tau_2} e^{-t/\tau_1} - \frac{1}{\tau_1} e^{-t/\tau_2} \right\} \right] \quad (19)$$

where P_N is nozzle pressure, Pa.

The fits for both Eqs 18 and 19, as shown in Figs. 8b and 8c, appear to be equally good and justify the use of the simpler first order model to represent the nozzle pressure response.

The best parameters for the fitted Eqs 17 to 19 are given elsewhere (28, 30). The linearity assumption implied by the transfer function modeling approach was verified for both the hydraulic and nozzle pressures (28). The study showed that the responses of the two variables were very rapid and are thus good candidates for controlling the injection phase.

Evaluation of Controllers

A simulation study was carried out to evaluate the performance of simple controllers using the dynamic models developed for the hydraulic and nozzle pressures (Eqs 17 to 19). The controllers chosen were the classical proportional, proportional-integral (PI), and proportional-integral-derivative (PID) types. The discrete recursive forms of the above control algorithms (Eqs 9 to 11) were used. The sample period was 5 ms., which is equal to that used in the dynamic tests (30). The controller parameters were tuned using the integral (ITAE) criterion (9), which gives a rapid response with a moderate amount of oscillation. The values of the parameters are given in Tables 2 and 3.

Two control loops were simulated: the first was control of the hydraulic pressure during the injection phase, while the second was direct control of

the nozzle pressure. The simulation loop is depicted in Fig. 3b, which shows that the process model represents the dynamics of the servovalve and the measured variable. The start of the injection phase was simulated by a step change in the set-point. Figure 9 gives the hydraulic pressure response using a proportional controller. It shows the improvement in response achieved by the controller compared to the open loop response. Different controller gain values were tried, and an improved response was obtained with a controller gain higher than that calculated by the ITAE tuning criterion. The offset or steady-state error typical of proportional controllers is decreased by increasing the controller gain, although too large a value causes overshoot and damped oscillations. The servovalve opening is shown in Fig. 9b and justifies the linearity assumption.

The hydraulic pressure response to the same step in set-point using a PI controller is shown in Fig. 10. The ITAE tuning criterion gives reasonable initial values for the controller parameters, but the response can be improved by changing either the controller gain, k_c , or the reset time, τ_I , or both. Near optimum response was obtained with $k_c = 0.15$ KPa/percent and $\tau_I = 0.03$ sec. The cost of improved performance is increased valve movement. The PID controller loop behavior is shown in Fig. 11 for the same situation. A marginally faster response, with a somewhat slower approach to the final value, is obtained. This controller is more sensitive to the controller parameter values as

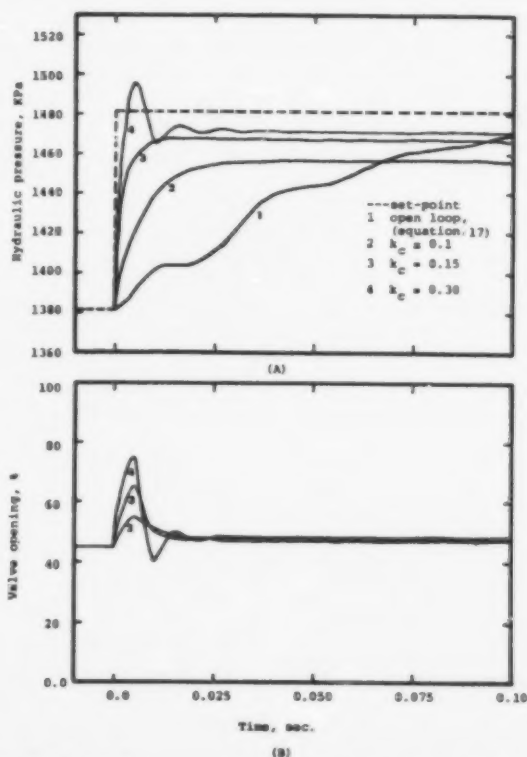


Fig. 9. Hydraulic pressure response to a step change in the set-point with a proportional controller.

Table 2. Controller Parameter Values (ITAE) For the Hydraulic Pressure Control Loop.

Controller	G_c	k_c	τ_I	τ_D
P	k_c	0.111	—	—
PI	$k_c \left(1 + \frac{1}{\tau_I S} \right)$	0.15	0.045	—
PID	$k_c \left(1 + \frac{1}{\tau_I S} + \tau_D S \right)$	0.145	0.058	0.003

Table 3. Controller Parameter Values (ITAE) for the Nozzle Pressure Control Loop.

Controller	G_c	Model	k_c	τ_I	τ_D
P	k_c	1st-ord.	0.021	—	—
		2nd-ord.	0.023	—	—
PI	$k_c \left(1 + \frac{1}{\tau_I S} \right)$	1st-ord.	0.018	0.048	—
		2nd-ord.	0.019	0.020	—
PID	$k_c \left(1 + \frac{1}{\tau_I S} + \tau_D S \right)$	1st-ord.	0.026	0.063	0.002
		2nd-ord.	0.027	0.026	0.001

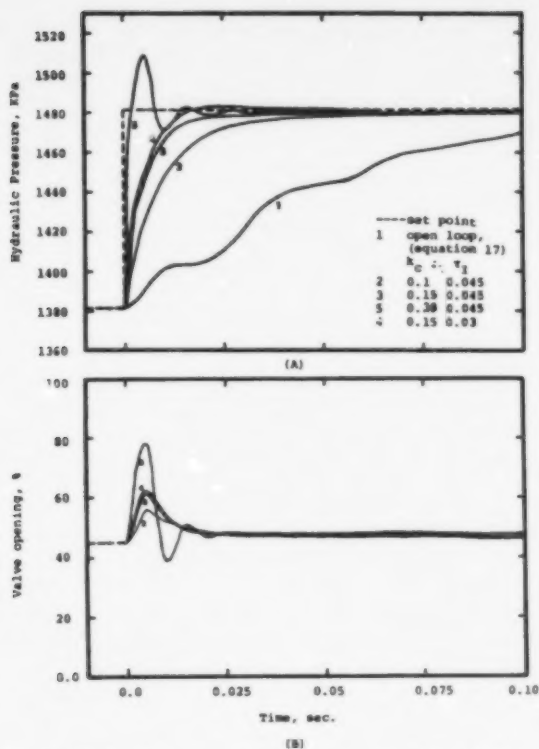


Fig. 10. Hydraulic pressure response to a step change in the set-point with a PI controller.

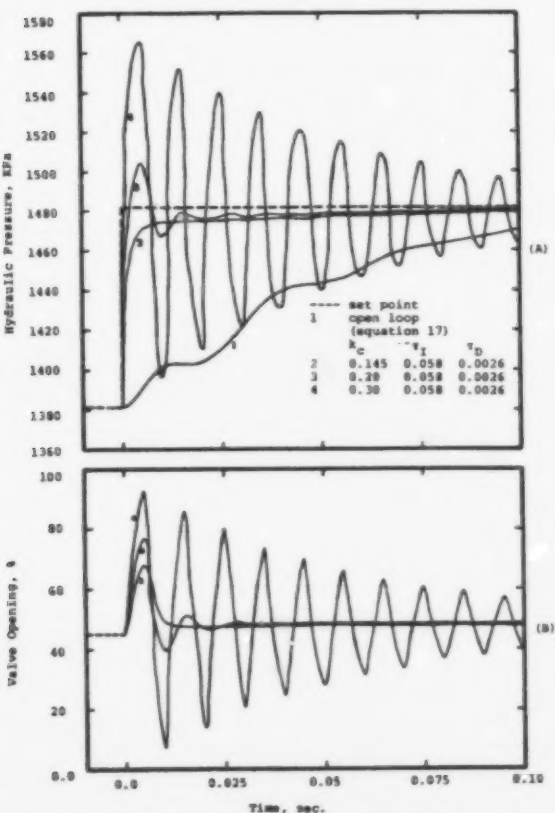


Fig. 11. Hydraulic pressure response to a step change in the set-point with a PID controller.

shown by the extremes of loop behavior as the gain, k_c , is varied from 0.145 to 0.3 (compare with Fig. 10). This sensitivity, coupled with only a slight improvement in performance over the PI controller, makes the latter the control algorithm of choice for controlling the hydraulic pressure. All three controllers effectively remove the servovalve induced oscillations seen in the open loop response. The proportional controller, although simpler to implement and tune, would only be used if the offset could be tolerated.

The flow into the mold is more directly related to the nozzle pressure than to the hydraulic pressure. The control of nozzle pressure directly (rather than via the hydraulic pressure) is of interest. Figure 12 shows the nozzle pressure responses to a step change in set-point pressure obtained from the nozzle pressure control loop simulation. The responses for the proportional, PI, and PID controllers are given together with the open loop response. The controllers were again tuned using the ITAE criterion, and their parameter values are given in Table 3. The PID controller has a clear advantage over the PI controller, in this situation, while the proportional controller gives the expected steady-state error. Some improvement in response could be obtained by adjusting the parameter values. However, this was not done at this stage.

Some responses to set-point-time pressure profiles were investigated for the PI and PID controllers. These are presented in Figs. 13 to 15. Figure 13 shows a simple ramping of nozzle pressure to a plateau followed by a decrease to the initial pressure. Both the PI and PID controllers perform about equally well in this service. The profile of Fig. 14 shows the nozzle pressure increasing (giving an increasing fill rate) at the beginning of injection. At $t = 0.2$ s, the profile is suddenly increased in a step fashion to correspond to filling a larger mold cross-

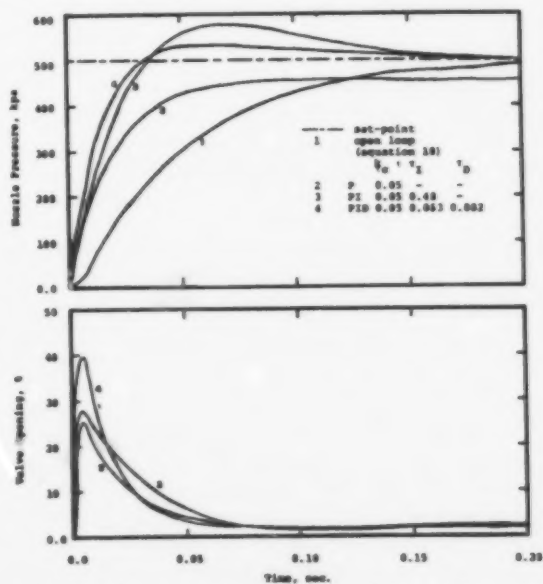


Fig. 12. Nozzle pressure response to step change in the set-point with proportional, PI, and PID controllers.

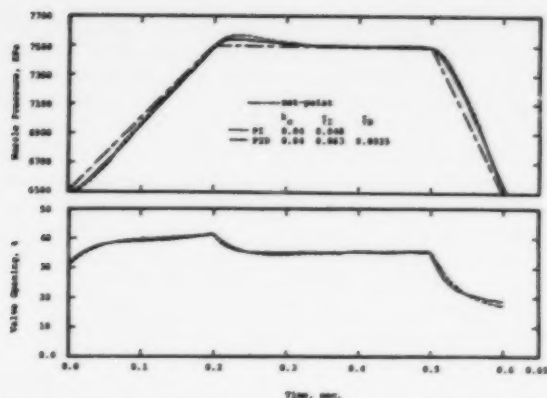


Fig. 13. Nozzle pressure response to a set-point-time pressure profile with the PI and PID controllers.

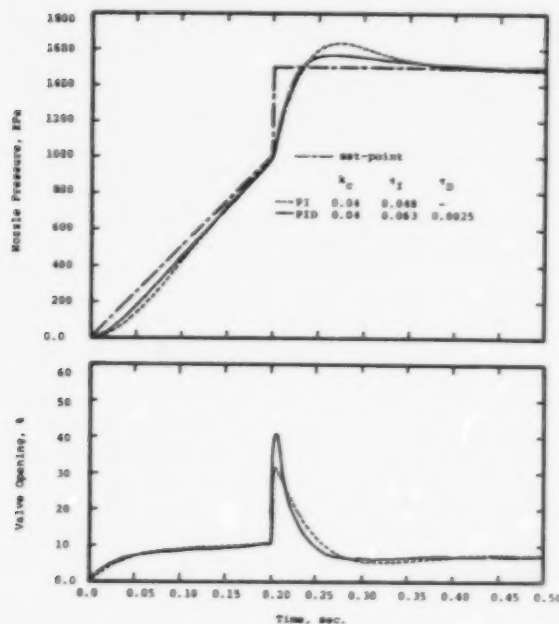


Fig. 14. Nozzle pressure response to a set-point-time pressure profile with the PI and PID controllers.

section. Both the PI and PID controllers handle the ramp part of the profile well, but the PID controller gives a better response to the step increase.

The profile of Fig. 15 shows a ramp to a plateau followed by a sudden decrease just prior to the packing phase. The PID controller again performs better than the PI controller, particularly for the sudden changes. Both controllers are not capable of regulating the pressure during the packing stage. This is seen from the large error during this phase, as well as the servovalve opening, which approaches 100 percent open. Such behavior is not due to a controller defect, but rather is symptomatic of demanding a performance of the hydraulic system of the injection molding machine that it is incapable of providing. Obviously, this is a situation to be avoided, but, unless the machine is correctly instrumented, it cannot be detected. Therefore, a

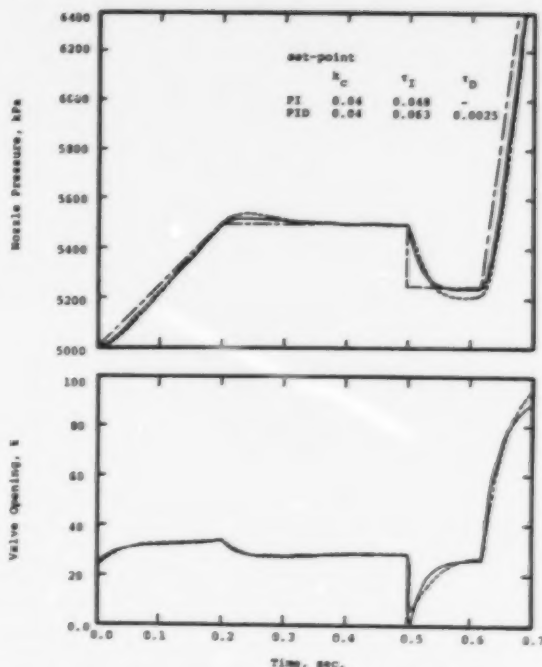


Fig. 15. Nozzle pressure response to a set-point-time pressure profile with the PI and PID controllers.

simulation such as this can give an indication of the inherent limits of operation of a given machine.

CONCLUSIONS

Simple pseudo-steady state relations between the hydraulic and nozzle pressures of an injection molding machine have been obtained and verified experimentally. One relation was based on a plane couette flow (PCF) approximation, while the other used the more complex annular couette flow (ACF). The ACF model gave slightly better results, but the PCF approximation is recommended because of its simplicity. These relations can be useful when attempting to control the nozzle pressure indirectly by controlling the hydraulic pressure.

Two control loops were simulated using proportional, PI, and PID controllers, tuned according to the ITAE criterion. One loop controlled hydraulic pressure, while the other controlled nozzle pressure. It was found that the PI controller gave the best overall performance. The proportional controller had an offset typical of this type of controller. The PID controller had slightly better conformance to the set-point changes, but was significantly more sensitive to controller parameter values that deviated from the optimum. It was found that a slight adjustment of the PI controller parameter values gave responses superior to those obtained using the ITAE tuning.

The control of the nozzle pressure simulation showed that the PID controller had better performance than the PI controller, particularly when rapid (step) changes in the pressure were demanded. Several nozzle pressure-time profiles were examined using the PI and PID controllers. The PID

controller showed generally superior performance compared to the PI controller. The proportional controller was not tried because of its characteristic offset. Neither the PI nor the PID controller could follow the profile during the packing stage since the profile demanded response beyond the capability of the injection molding machine.

All the controllers, in both loops, gave responses that were about an order of magnitude more rapid than the open loop response. In addition, all the controllers were capable of removing the servo-valve induced oscillatory component seen in the open loop response of the hydraulic pressure.

REFERENCES

1. K. J. Astrom and P. Eykhoff, *Automatica*, **7**, 123 (1971).
2. R. E. Nieman, D. G. Fisher, and D. E. Seborg, *Int. J. Control*, **13**, 209 (1971).
3. I. Gustavsson, *Automatica*, **11**, 3 (1975).
4. D. R. Coughnower and L. B. Koppel, "Process Systems Analysis and Control," McGraw-Hill, N.Y. (1965).
5. W. L. Luyben, "Process Modelling, Simulation and Control for Chemical Engineers," McGraw-Hill, N.Y. (1973).
6. A. J. Young, "An Introduction to Process Control Systems Design," Longman Green, N.Y. (1955).
7. G. E. Box and G. M. Jenkins, "Time Series Analysis: Forecasting and Control," Holden-Day, San Francisco (1976).
8. P. Eykhoff, "System Identification," John Wiley, London (1976).
9. C. L. Smith, "Digital Computer Process Control," Intext Educational Publisher, N.Y. (1972).
10. J. G. Ziegler and N. B. Nichols, *Trans. ASME*, **64**, 759 (1942).
11. D. H. Harry and R. G. Parrot, *Polym. Eng. Sci.*, **10**, 209 (1970).
12. J. L. Berger and C. G. Gogos, *Polym. Eng. Sci.*, **13**, 102 (1973).
13. M. R. Kamal and S. Kenig, *Polym. Eng. Sci.*, **12**, 294 (1972).
14. M. R. Kamal and S. Kenig, *Polym. Eng. Sci.*, **12**, 302 (1972).
15. J. L. White, *Polym. Eng. Sci.*, **15**, 44 (1975).
16. H. A. Lord, *Polym. Eng. Sci.*, **19**, 469 (1979).
17. K. K. Wang, *et al.*, Cornell Univ., Progress Report #6 (1979).
18. P. G. Lafleur and M. R. Kamal, *Adv. Plast. Tech.*, **1**, 4, 8 (1981).
19. A. Shankar and F. W. Paul, *ASME Trans.*, **104**, 86 (1982).
20. H. T. Plant and R. T. Maher, *SPE ANTEC Tech. Papers*, **21**, 74 (1975).
21. C. Y. Ma, *Polym. Eng. Sci.*, **14**, 768 (1974).
22. J. W. Peter, *SPE ANTEC Tech. Papers*, **18**, 847 (1972).
23. M. A. Davis, *SPE ANTEC Tech. Papers*, **22**, 618 (1976).
24. J. Border and N. P. Suh, *SPE ANTEC Tech. Papers*, **28**, 323 (1982).
25. M. R. Kamal, I. Patterson, and D. Abu Fara, *SPE RETEC*, NJ, (1983).
26. A. Haber, M. Eng. Thesis, McGill University, Montreal (1982).
27. Anon, "Moog A076 Servovalve Technical Manual," Moog Inc., Industrial Division, New York.

28. D. Abu Fara, M. Eng. Thesis, McGill University, Montreal (1983).
29. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," John Wiley and Sons, N.Y. (1960).
30. M. R. Kamal, I. Patterson, D. Abu Fara, and A. Haber, *SPE ANTEC Tech. Papers*, **29**, 658 (1983).

DISCUSSION: DIB ABU FARA, M. R. KAMAL, AND W. I. PATTERSON

H. Winter: I would like to comment on the pressure transducers. You mentioned that you had some problems with the response time. The long response time of the transducers that operate on strain gages is due to the processing of the signal within the controller unit. If you strip the transducer and feed a 6V excitation voltage from a dc power supply and take the output signal directly, that will minimize the delay. We have used this on an extruder where we could record the passing of the flight. Have you tried anything like this?

I. Patterson: That's what we are doing. The transducers are Dynisco and are fed with a 6V excitation voltage and the output signal goes directly to the a/d converter. The difficulty for the nozzle or anything within the cavity is due to the long capillary connecting the measuring diaphragm to the diaphragm on which the strain gages are mounted. Essentially it is a transport lag as the mercury gets pushed from the first to the second diaphragm. I think the response times are of the order of a few milliseconds. I don't see, given the type of construction, how you can do better than that. A technique needs to be developed where the measuring element can be mounted directly on the measuring diaphragm. I agree that the manufacturers signal processing introduces a lag in the hundreds of milliseconds since the signal is highly damped for display and/or readout purposes.

J. Wallace: When you mentioned other types of controllers you'll be going on to, did you mean a PID controller? What else did you have in mind?

I. Patterson: Things like dead-beat controllers, self-tuning regulators, etc. In other words, something that combines online process model estimation so that if the process changes the best values of the parameters are always being identified. Essentially the controller is constantly being retuned in some optimum sense, so that even if the process drifts with time the performance of the control loop does not degrade.

PANEL DISCUSSION

M. E. Ryan: I have frequently found that very stimulating and interesting discussion occurs at the end of the day during the general discussion session where people from industry make various comments and inputs as to how mathematical modeling could be used, should be used, or cannot possibly be used. This informative exchange is mutually beneficial to all participants. As a consequence, we decided this year to try to integrate this dialogue into the program. There will be three semi-formal presentations from individuals with different backgrounds and involvement in polymer technology and mathematical modeling, which should serve to catalyze a more vigorous discussion and exchange of ideas. The three panelists are Mr. George Salloum, Industrial Materials Research Institute, National Research Council of Canada; Mr. Rob Winton, Structural Dynamics Research Corporation; and Mr. Jim Wallace, Esso Chemical Canada.

G. Salloum: I will talk briefly about: the worldwide computer-aided mold design systems in injection molding, computer-integrated injection molding, and how modeling techniques can be used in the industrial environment.

Eight different application software systems may be considered. Basically, I don't see much competition between these packages since each one focuses on a particular aspect of injection molding. For example, the DUCT program, which was jointly developed by Cambridge University and the CAD/CAM center in Great Britain, is primarily concerned with the design and machining of the mold components. Moldcool is concerned with cooling analysis and is available from Application Engineering Corp. in the United States. CAD-M is concerned with computer-aided design, drafting, and manufacturing and was jointly developed by Matsushita Electrical Industrial and the University of Tokyo at the end of 1978. TMC is tooling and molding cost, which was developed in Italy by DME and the Plastics and Computer Company, and is available on the General Electric Information System. Moldflow has been developed in Australia and deals essentially with the melt flow analysis in the mold. Moldflow is now offered as an integrated package on a few CAD/CAM systems available on the market. Optimold was developed by Graphics Technology Corporation in collaboration with Cornell University. However, no two of these systems have been designed for exactly the same purpose. In order to cover all aspects of the injection molding process, at least half of these programs would have to be used. Many other programs and packages have been developed, but for various reasons are not being marketed commercially. It should be kept in mind that in the United States there are about

33,000 companies involved in injection molding. Approximately half of these may be in the position of buying some sort of CAD/CAM system.

The Industrial Materials Research Institute has developed a strategic plan to define directions and targets for the implementation of CAD/CAM technology in injection molding. The critical aspect is for the user to be able to easily interact with the system for applications in mold design, layout, product design, product analysis, flow analysis, thermal analysis, structural analysis, and simulation of the manufacturing process. We are trying to integrate these various components into a single data base. These components include information on products, materials, processes, and molds, along with a variety of analytical tools.

The kind of information that is required to achieve this goal is related to a specified level of automation. Some tasks could be completed automatically, whereas others may not. According to the type of application, we have developed the necessary information. For example, in the materials data base we need the physical properties of the polymer as well as mathematical expressions or models for these properties. Similar information is also required for the materials used in the construction of the mold. Properties of the coolant fluids are also included. Group technology is being used as a basis for structuring this information. In terms of tooling, we have information on feeding systems much as the sprue, gate, and runner configurations (General Electric currently offers a DME mold base selector).

The essential element is to integrate these various capabilities. The systems commercially available today are not reaching a broader base in the manufacturing environment because they lack this integrated structure. The user must therefore deal with multiple sources of information and suppliers. This implies an expensive process and reliance on different data bases.

Within the near future we should be able to start with a solid model of the component, visualize the part with all the corresponding mass properties, select a candidate material, develop a dynamic model of the process, perform the simulation, and conduct a structural analysis of the part. If the product specifications are not satisfied, the user can make modifications or redesign the part. The cost of the product can then be determined, along with the optimum number of cavities and optimum press size and capacity. Once these decisions are made, the user can proceed to the mold layout, design the mold from the tool component data base, and optimize the cooling circuit design and operating conditions. The final stage is the generation of the bill of materials. Many companies are targeting the

development of such a system within two or three years, not only in regard to injection molding but also in the aerospace and automotive industries.

Some of the capabilities that we have at IMRI in order to achieve this task include a VAX-based data management system with a basic editor and graphics package linked to the surface modeling, solid modeling, finite element analysis package, flat pattern development, numerical control, and bill of materials.

R. Winton: I am pleased to have the opportunity to share with you some of the new and exciting technologies that SDRC has been involved with over the last few years. We have a joint venture with General Electric. SDRC is an engineering consulting company that has a large R & D division, which over the past 16 years has been in the forefront of finite element analysis and solids modeling. We have now integrated our solids modeling and finite element work with the injection molding business and we provide turn-key services to U.S. and Canadian plastics manufacturers. We start with new product design; we do a complete simulation using solids modeling and utilize Moldflow and Moldcool to examine the manufacturing issues, automatic selection of bill of materials for the die parts, and thermal analysis to develop the cooling circuit configuration. We communicate electronically with CGE's machining division in Cobourg, Ontario, where the mold parts are automatically machined.

J. Wallace: One of the areas we have been involved with is that of control simulation. You can do simulations to determine conditions where you can no longer hold the reactor stable. This is useful since carrying out the experiment in practice is generally not feasible. It is possible to determine whether the venting specifications are adequate. The handling of very active initiators is another area where simulation can be extremely useful. These initiators generally require storage at low temperature. In the design of automated initiator handling systems, which will be safe in all foreseeable circumstances, it is necessary to understand the kinetics and energetics of the system. Otherwise self-accelerating decomposition may occur, resulting in fire or explosion.

We were able to simulate the observed auto-accelerating decomposition in a small vessel, and to provide a means for evaluating the risk potential for a full sized installation. The importance of initiator concentration and the effect of vessel size and heat-transfer coefficients could readily be observed.

Consider the case of a polymer manufacturer providing technical service to his customers. Simulations have been of value in the case of new equipment design or costly modification to existing equipment. In the area of assistance with customer's day-to-day problems, there may exist a large technical service laboratory which is well-equipped with extruders, single and twin screw, a film-blowing line, blowmolding, and injection molding facil-

ities, etc. Material processability and behavior is often directly evaluated using this equipment rather than by doing a simulation. The practical response to a customer in a technical service situation is that he wants to know what to do in this particular situation, and you don't have the luxury of time to develop a simulation. The customer situations that arise cover an enormous spectrum, and to have a general-purpose simulation to cover all contingencies is hard to imagine.

Extremely good documentation of programs is necessary to avoid the so-called "gypsy-programmer syndrome"; you have a powerful program but nobody knows how to use or modify it because the person who developed the program has left, or the company that sold the program is no longer in business. Also, the learning time for using a program can be considerable.

The important thing is to find programs that are as simple as possible that can simulate, to some extent, actual circumstances and can be readily modified as experience is gained.

Once these have been successfully used, more enthusiasm will develop. Management is somewhat hesitant about programs that could consume vast amounts of time and money and then are terminated before they can achieve any practical level of return. Simple, effective programs are likely to be the best received.

GENERAL DISCUSSION

R. Gauvin: I have three questions for Rob Winton. First, your company seems to be quite capable in helping the product designer. In your opinion, what other North American companies are in a similar position?

R. Winton: There are really very few. There was a benchmark done by Texas Instruments around September of last year and the keyboard example I talked about was part of the benchmark they had done. They invited eight companies to partake and only ourselves and one other accepted the challenge. I believe that the other company took six months to get to the final mold design. Based on Texas Instruments there may only be ourselves at this point. But it won't take long for other companies to attain this capability.

R. Gauvin: Second, are you actually developing the software and, if so, what kind of specialists are doing this?

R. Winton: Let me explain a little more about the background of SDRC. Our corporate division has an R & D staff of about 100 who are dedicated to software development. Most of those people are computer scientists and engineers. The company is not just involved in the injection molding analysis business; that is just one segment. We are involved in engineering mechanics and engineering dynamics in general. We are heavily involved in the aerospace business, the Canadian energy industries, and in element modeling, etc., which is developed

in our technical staff group. We have two divisions: SDRC, Inc., which is the consulting division I am part of, and the joint venture company General Electric CAE International, which is half owned by SDRC and half owned by GE.

R. Gauvin: Finally, with the modeling techniques that you now have available, how many times have you been able to avoid prototyping?

R. Winton: This integrated technology that I showed has only been used in a consulting fashion for about a year now. The first major project was in February of last year. The last two or three major turnkey projects that have been done were done without the need for prototyping. The first couple of times the end user wanted to have the assurance that he could at least meet his tooling deadlines. The real benefit to the industry is the bottom line dollars and cents. We can develop a proven design in about 30 percent less time than the conventional method and much less costly. Most of the projects we have done are fairly large turnkey designs where we have taken full responsibility for the product design and then subcontracted to Canadian General Electric in Cobourg, Ontario, the actual machining and delivery to the end user of the entire system, with 100 or so sample parts of each component of the assembly.

M. R. Kamal: Mr. Salloum said that there are 33,000 injection molding companies in the United States. He estimated that within a couple of years about half of them would use CAD/CAM systems. In the framework of 1990, how many of these companies would have acquired, not just used as a service, these kinds of systems?

R. Winton: We've just been going through the same kind of estimate. We're forming a joint venture company in Ontario to allow the small Ontario plastics companies access to the system without them having to purchase the equipment themselves. The studies we've done indicate that probably no more than 20 percent of all the large plastics manufacturing companies will eventually purchase full-scale systems themselves. There is more than just the capital investment consideration. The training of the personnel and use of the system is not trivial. Our engineering staff consists of professionals who have been involved in plastics injection molding for 20 to 25 years and have broad experience so that they can interpret what the computer generates. If you try to interpret the output in a simple manner you may make mistakes. The total software package is approximately \$200,000 CDN, then you need a VAX system, and finally a significant investment in the training of your people. Therefore, not everybody can afford to get this kind of system and probably only the large Fortune 500 companies will.

G. Salloum: You have described the situation as it exists today. The goal we are striving for is how to simplify or reduce the cost of these systems and make them available to the medium or small-sized companies. A few years from now I think that the \$200,000 package may be available for \$50,000.

M. E. Ryan: I would like to comment on the role that many of us at this meeting might play in this particular area. One role that industry can play at the present time is to inform us about the successes or shortcomings of the commercially available systems through known case histories. Unfortunately, the practical experience with different products is not widely publicized or disseminated in the open literature. However, I think that this is an important role that industry can play in evaluating these systems and informing us where the major difficulties or limitations are and where improvements need to be made. There is a role for academic research to play in the development of more efficient and accurate software with broader capability. The entrepreneurs deserve the credit for having made some software packages available in a marketable, user-friendly format that can be used currently. There is a need for interaction and dialogue between these various groups. There is certainly a need to reduce the cost with these systems. Even for large companies the cost-benefit analysis or cost justification for these systems is difficult. The smaller companies, who can not afford this capability, are worried about remaining competitive. These systems should be made available to the small or large, custom or captive molder in order to improve the industry generally and make it more competitive.

R. Winton: Last October we held a users conference where we brought in six of our large clients that we have been working with during our first formative year. Each of these clients described to the audience their experiences in using this technology in comparison to the way that they would have done it in the past. Copies of this conference are available from us. The question of making the technology available to smaller firms has also been a concern of SDRC. We are looking into the formation of a joint venture operation that will be tied into the Ontario plastics industry so that we can provide very low cost consulting expertise to companies having fewer than 50 or 100 employees who cannot justify the purchase of the hardware, software, and training.

R. Gauvin: At IMRI/IGM we are developing a databank for various plastics materials. How cooperative will the material suppliers be in providing us with physical property data? What is the general industrial attitude?

J. Wallace: I think that, in general, the material suppliers would be very happy to provide as much information as possible on their materials.

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● STUDENT MEMBER

Annual Dues: whenever joining \$8.00 (no initiation fee; not pro-rated)

● REINSTATED MEMBER

Annual Dues: whenever reinstated \$45.00 (no initiation fee; not pro-rated)

I wish to join the _____ Section.

REFERENCES: The Bylaws require the names of three references who are familiar with your work. One of them should be a member of the Society. Assistance in providing member-references will be given on request. Signatures are not necessary.

1. (Member-Sponsor) _____
2. _____
3. _____

STATEMENT OF COLLEGE WORK

Years attended		Institution	Major	Degree	Education Credits
From	To				

RECORD OF QUALIFYING EXPERIENCE IN PLASTICS

DATES				Give your title, name and location of employer. List in chronological order. Describe duties fully and state any important engineering work you have done in each position. If space is not sufficient, use separate sheet.	Time in years (a)	% in plastics (b)	Qualifying experience (a x b)
From Mo.	Yr.	To Mo.	Yr.				
					yrs./mo.		yrs./mo.

CREDENTIALS COMMITTEE APPROVAL ONLY Approved Grade

(S)	Date
(S)	Date
Office use only:	Division
ID#	Job Class
Grade	Date Elected
Section	

SUB-TOTAL

Total education and experience credits. ►

I certify that the statements made in this application are correct. I agree, if elected, to be governed by the Constitution and Bylaws of the Society and to promote the objectives of the Society.

Signature in ink.

Date

If applying for Member or Senior Member, please complete *in detail*:

STATEMENT OF COLLEGE WORK					
Years attended		Institution	Major	Degree	Experience Credits (see notes below)
From	To				

RECORD OF QUALIFYING EXPERIENCE IN PLASTICS

DATES				Give your title, name and location of employer. List in chronological order. Describe duties fully and state any important engineering work you have done in each position. If space is not sufficient, use separate sheet.	Time in years (a)	% in plastics (b)	Qualifying experience (a × b)
From		To					
Mo.	Yr.	Mo.	Yr.				
					yrs./mo.		yrs./mo.
SUB-TOTAL							
Total education and experience credits. ►							

Grade	Requirements
Senior Member	Minimum of twelve (12) experience credits and current continuous membership in the Society for a minimum of two (2) years.
Member	Minimum of six (6) experience credits.
Affiliate Member	Less than six (6) experience credits.
Student Member	Regularly enrolled FULL-TIME student in a course of study in plastics.

CREDENTIALS COMMITTEE APPROVAL ONLY		Approved Grade
(S)	Date	
(S)	Date	

Experience Credits

Grade of Membership . . .

Membership grades are based on experience credits which are earned as follows:

1. Experience credits earned for education.

Maximum credits allowable for education shall be six (6). Use highest degree credits ONLY.

Doctorate in science or engineering	6 credits
Masters in science or engineering	5 credits
Bachelors in science or engineering	4 credits
Any degree other than above	2 credits
Associate or Adjunct in Plastics	2 credits
Associate or Adjunct (awarded by Community College or equivalent for two-year course of studies, without specializing in plastics).	1 credit

When filling in the "Statement of College Work" above, place the

corresponding number of credits earned in the right-hand column.

2. **Experience credits** are determined by the proportion of time involved in actual technical and engineering duties in plastics for each position held. For instance, if only three of the five years you worked for the XYZ Co. comprised technical or engineering duties, then three (3) years (60% of 5 yrs.) would constitute the "Qualifying Experience" you would enter in years and months in the right-hand column under "Record of Qualifying Experience in Plastics."

Please detail carefully the engineering skill required for each position to help the Credentials Committee judge experience as "qualifying."

When you have determined the number of credits which you believe you have earned, consult the following member grade requirements. Indicate on the reverse side the grade of membership for which you believe you are qualified.



INFORMATION FOR AUTHORS

Submission of original and review articles is encouraged. There is no limit on length. Three copies of the manuscript should be submitted, which should be typed, one side only, double space, with at least a 1-inch margin. Submission will be taken to imply that the paper has not been previously published, that it is not being considered elsewhere for publication, and that if accepted it will not be published elsewhere in the same form, in any language, without the consent of the editor or publisher. Authors must agree to transfer copyright to the publisher when an article is accepted for publication. Unless notified to the contrary by the authors, the publisher assumes that the act of submitting the article signifies the authors' agreement to such copyright transfer to the publisher. The journal carries a voluntary page charge. Each manuscript should include:

A separate title page, headed by a concise, meaningful title (avoid abbreviations) for the paper. This page should provide:

- The name and affiliations of each contributing author at the time the paper was prepared.
- Indicate by asterisk any changes of address for each author since article preparation.
- Acknowledgment of any prior oral presentation and original source of the material.

A separate abstract page, consisting of a single paragraph of 100–200 words to include the title and the names and addresses of the authors. Define any abbreviations for substances or methods (such as ABS, SAXS, etc.).

A list of references, on a separate page at the end of the text, numbered in order of text citation. The references are to be abbreviated in the form used in Chemical Abstracts using the names of all authors preceded by initials; see Bibliographic Guide for Editors and Authors, American Chemical Society, Washington, D.C.

- Within the text, the reference citations are typed in parentheses in line with the main copy (no superscripts or subscripts), thus:

According to Young, et al. (1)...

- In the list of references the general style is as follows:

For periodicals:

1. S. S. Young, J. L. White, E. S. Clark and Y. Oyanagi, *Polym. Eng. Sci.*, **20**, 798 (1980).

The journal name and volume are to be underlined and the year is placed in brackets. The issue number is given only when needed for identification. The article name is eliminated unless the reference is unclear without it.

For books: The title to be spelled out in full.

5. H.-G. Elias, "Macromolecules," Ch. 1, Vol. 2, Plenum Press, New York (1977). (Include the state when the city is not identifiable.)

A list of nomenclature, identifying symbols and abbreviations, commonly desirable at the end of the text. Footnotes are to be avoided.

Equations, numbered and typed in the appropriate place in the text. Where symbols cannot be typed, write them neatly in ink.

Tables, each typed on a separate page, with a heading, and numbered with arabic numerals that correspond to the order in which they are cited in the text. The tables should be inserted in the manuscript after the references and before the figures.

Figures, assembled at the end of the manuscript and preceded by a typed list of captions that explain them. Please also supply a set of original figures or sharp glossy photos thereof, on 8½ × 11 paper or attached to sheets of this size, one sheet for each figure. Each should be identified on the front edge or on the back (photographs) with the name of the first author and the figure number (e.g., Smith, Fig. 1). Originals are to be prepared with high contrast India ink and to bear uniformly stencilled notations. Line drawings and photos should be of a quality suitable for good photographic reproduction and retained legibility upon size reduction to one quarter. Manuscript transmittal letter should indicate if the figures need be returned.

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Society of Plastics Engineers
14 Fairfield Drive
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